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Anushka Gangnaik, Yordan M. Georgiev, and Justin D. Holmes

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Correlation of lithographic performance of the electron beam resists SML and ZEP with their chemical structure

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Study of topographical and structural changes occurring in a positive resist known as SML after electron beam lithography are presented in this article. The authors also defined its chemical structure, which is very important for understanding the lithographic performance of the resist. The structural and lithographic properties of SML have been compared to the traditional ZEP resist. First, the change in the surface roughness with respect to the electron dose of SML and ZEP resists was measured. It was found that both resists start off with similar initial roughness values. However, ZEP was observed to have a higher roughness at the apex electron dose, thereafter a reduction in roughness was observed. The roughness variation in the two resists reflected on the resolution of the gratings that were patterned in both the resists. Gratings in SML showed smoother line edge roughness, and the patterns transferred using SML resist showed more even features than the ones transferred with ZEP. Subsequently, to understand the chemical composition of the new resist, Fourier transform infrared spectroscopy (FTIR) measurements were performed on both the resists as well as on poly(methyl methacrylate) (PMMA) and their spectra were compared. The FTIR spectra revealed that SML had a chemical structure similar to ZEP and PMMA polymers. The high sensitivity of ZEP is attributed to the Cl group in the compound, which is not present in SML and PMMA and can therefore explain their lower sensitivity to electron exposure in comparison to ZEP. Unlike PMMA but comparable to ZEP, SML shows an IR peak at a wavenumber close to 850 cm\(^{-1}\), suggesting the presence of \(\alpha\)-methylstylene group within its chemical structure, which accounts for the resist’s high etch durability, similar to ZEP. Additional FTIR measurements of pre- and postexposed resists together with their attributions to the resolution of the SML and ZEP resists is also demonstrated in this article. The data presented in the study highlights the chemical properties of SML and ZEP resists polymers and correlates them to their lithographic performance. © 2015 American Vacuum Society. [http://dx.doi.org/10.1116/1.4926387]

I. INTRODUCTION

Electron beam lithography (EBL) is one of the most reliable nanolithography techniques. EBL resists are specially formulated to respond to a highly focused beam of electrons. Therefore, a chemical change occurs in the resist and radiated regions are selectively removed (positive tone) or left behind (negative tone) by resist tone-specific developers. The lithographic performance of any electron beam (e-beam) resist is affected by various factors such as the electron energy, resist thickness, substrate material, developers, development time, and temperature. To extract the prime performance from resists, various resolution enhancement practices are constantly being employed. Many new resists are also being formulated to achieve ultrahigh resolutions.

Line edge roughness (LER) of patterns is recognized as a nontool related limiting factor of the resist resolution.\(^1\) The LER effects, especially below 50 nm, become dominant and start to hinder sharpness and stability of the structures. At such a small scale, the surface (side wall) roughness arises due to the size of resist polymer molecules (molecular weight) and molecule aggregates. These granular aggregates determine the quality of structures and the resolution of the resists.\(^1,2\) During the e-beam exposure, the proximity effect will cause the close regions to receive a small dose, which will partially developed during development and thus give rise to the LER. At narrow spacing like 5–10 nm in positive resists, short-range intermolecular forces between the exposed and unexposed resist may obstruct the exposed polymer molecules in this region from dissolving in the developer solution.\(^3\) This can also account for irregularities on the edges of fine structures. Many previous experiments and simulations have shown that roughness also arises during the development process of the resist features.\(^4,5\) Use of ultra- or megasonication during development assists the polymer molecules to overcome the intermolecular forces and dissolve in the developer solution.\(^3,6\) The use of 7:3 isopropyl alcohol (IPA):water developer over the conventional 1:3 methyl isobutyl ketone:IPA developer has shown to reduce the LER of poly(methyl methacrylate) (PMMA) greatly.\(^7\) The highest resolution EBL resist commercially available is hydrogen silsesquioxane (HSQ), but this resist also suffers LER issues. Being a negative resist, HSQ forms aggregates of the polymer molecules which determine the roughness of structures.\(^1,2\)
In our previous work, we investigated the lithographic performance of the novel SML resist and compared it to traditional high resolution ZEP and PMMA resists. In the present paper, we extend our investigation on the surface roughness of the new resist and its effect on the resolution of SML. First, the variation in surface roughness of SML and ZEP with respect to e-beam dose is determined. Subsequently, high resolution gratings were exposed on the two resists to compare the LER.

The work also included studying the chemical structure of SML, as well as on the changes occurring in the SML structure after e-beam irradiation, in an attempt to correlate them to the lithographic performance of the resist. Fourier transform infrared spectroscopy (FTIR) methods were employed to determine the chemical composition of SML and compare to that of ZEP and PMMA resists. Since ZEP and PMMA are widely studied, this comparison helps to better understand the lithographic behavior of a new resist.

II. EXPERIMENT

 Silicon wafer of (100) orientation was diced into 10 x 10 mm chips for all the experiments to keep the resist distribution equivalent. SML resists of various concentrations was acquired from EM Resists Ltd, ZEP 520A was purchased from Nippon ZEON Corporation and 950K PMMA A7 from MicroChem Corporation.

 Contrast curves were obtained for SML, ZEP, and PMMA by spinning down ~300 nm of the resists on the Si chips, SML and PMMA were baked at 180 °C and ZEP at 120 °C for 180 s. Boxes of 50 x 50 μm were exposed on all the resists at 10 keV from 0 to 150 μC/cm². SML and PMMA resists were developed using 7:3 IPA:water developer for 15 s followed by a 15 s pure IPA rinse. ZEP resist was developed in its standard ZED N50 developer for the same time and rinsed with SML/PMMA. All the EBL exposures were carried out on Raith e-LiNE Plus. The step height in the resist was measured using a DEKTAK Profilometer.

 For writing the high resolution gratings, film thickness of 50 nm was chosen for SML and ZEP resists and single pixel lines were written on them with pitch sizes of 40, 60, 80, 100, and 200 nm by 30 kV e-beam voltage, 2 nm step-size and 10 μm aperture size. They were developed in the appropriate developer solvents that were kept at 0 °C to enhance the resolution. The substrates were cameras on Raith e-line Plus and FEI Helios NanoLab 600 at 10 and 5 kV, respectively. Before imaging, all the substrates were coated with a very thin layer of Au/Pd.

 To relate the LER of the resist structures that were transferred into the Si substrate, above mentioned high resolution gratings were etched for 1 min using inductively coupled plasma Etcher (surface technology systems) with SF6 and C4F8 gas mixture. For the metal lift-off process, 5 nm thick chromium metal layer was deposited on similar high resolution gratings using electron beam evaporation in a Temescal FC-2000 machine. The lift-off was performed by immersing the developed resists into Microposit 1165 remover (Shipley) for 5–10 min. They were then rinsed under flowing de-ionized water and blow dried with N2.

 The surface roughness of the exposed and unexposed resists was measured by using tapping mode in an atomic force microscope (AFM) (Park systems, XE-100) under ambient conditions. The LER of the gratings was acquired by processing the scanning electron microscope (SEM) images with imageJ software. The 3σ standard deviation of single lines was gained by processing the SEM images that are illustrated further in the article. To obtain infrared spectra of SML, ZEP, and PMMA resists, FTIR was used. The spectra were collected on Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with an attenuated total reflectance accessory (Harrick Scientific).

III. RESULTS AND DISCUSSION

A. Roughness measurement

 In order to determine the change in surface roughness with respect to increasing e-beam dose, it was first necessary to determine the processing dose range of the SML and ZEP resists. Hence, contrast curves were obtained for both the resists and are shown in Fig. 1(a) (contrast curve of PMMA is for a later discussion). The contrast curves show that the sensitivity of ZEP is almost five times higher than that of SML, while the contrast value γ is slightly lower (γ = 12 for SML and γ = 11 for ZEP). The root mean square (RMS) values of surface roughness for the two resists at different e-

![Fig. 1. (Color online) (a) Contrast curves of SML (blue triangles) and PMMA (red diamonds) developed with 7:3 IPA:water and ZEP (black squares) developed in ZED N50; (b) RMS surface roughness of SML and ZEP.](image-url)
beams are presented in Fig. 1(b). They were measured by AFM on the same boxes where the contrast curves were obtained. As expected, the roughness of both resists tended to increase with increasing dose until a certain dose value. As the e-beam dose is further increased, the roughness reduced equivalent to the initial value. The roughness versus dose curves of both the resists is very similar to that of PMMA, which is reported elsewhere. The certain level of roughness of a polymer resist can be determined by various factors such as phase separation, polymer aggregation, molecular weight of the polymer, developer solvents, and development time. In this study, we related two such reasons for the roughness behavior of the resists observed in Fig. 1(b). First, it was suggested for PMMA that the roughness originates during the polymer phase separation while developing the resist after e-beam exposure. The bell-shaped curve of the RMS roughness versus e-beam dose arises due to the different rate of phase separation occurring at various exposure doses. Since SML and ZEP show similar bell shaped curves, the phase separation processes in both resists taking place during development may be similar to that of PMMA; however, the mechanisms might differ because of the different developers used.

Although the roughness of both the resists (SML and ZEP) commenced with similar values, as the dose increased the roughness intensities tended to differ, as shown in Fig. 1(b). On reaching the maximum roughness, ZEP displayed a rougher surface with an RMS value of 13.2 nm, whereas SML had an RMS value 10.5 nm. The lower surface roughness of SML compared to ZEP is beneficial from a lithographic perspective since surface roughness of the side walls of exposed structures eventually determines their LER. We suggest that this difference in roughness is due to the difference in molecular weight of the two resist polymers. The size of the radius of gyration of a polymer is also responsible for the roughness. Thus, the smaller the radius of gyration, the lower surface roughness is observed, and this is the second possible reasoning for the roughness behavior of the resists observed in Fig. 1(b).

To visualize this, two points, A and B, from the roughness versus dose curves in Fig. 1(b) were chosen for a comparison. The AFM image in Fig. 2(a) illustrates the topography of ZEP resist at point A, whereas Fig. 2(b) shows the topography of SML resist at point B. Points A and B are the doses at which maximum surface roughness was observed for the two resists. By comparing both images, the topography of the ZEP resist is more uneven and blotchy than that of SML, which is reported elsewhere. The certain level of roughness of a polymer resist can be determined by various factors such as phase separation, polymer aggregation, molecular weight of the polymer, developer solvents, and development time. In this study, we related two such reasons for the roughness behavior of the resists observed in Fig. 1(b). First, it was suggested for PMMA that the roughness originates during the polymer phase separation while developing the resist after e-beam exposure. The bell-shaped curve of the RMS roughness versus e-beam dose arises due to the different rate of phase separation occurring at various exposure doses. Since SML and ZEP show similar bell shaped curves, the phase separation processes in both resists taking place during development may be similar to that of PMMA; however, the mechanisms might differ because of the different developers used.

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peaks are missing in the PMMA spectra in Fig. 7(a). The phenyl rings and the Cl groups of ZEP, respectively. These were carried out on 150–60 nm thickness on Si substrates. The measurements conducted on thin SML, ZEP, and PMMA films having were published. Hence, to understand the similarities of the new area similar. ZEP is a modification of the PMMA polymer. Since, those with SML resist as seen in Figs. 4(c) and 4(d). The grating etched into the Si substrates also show similar results. Even though relatively smooth lines were obtained after EBL exposure with ZEP [Fig. 3(a)], the LER of the gratings seemed to degenerate after etching, possibly due to the higher surface roughness of ZEP as compared to SML. Thus, a higher LER was observed in patterns transferred by using ZEP resist in comparison to SML.

B. FTIR measurement

Figure 5 illustrates the FTIR measurements that were conducted on thin SML, ZEP, and PMMA films having 50–60 nm thickness on Si substrates. The measurements were carried out on 1 × 1 cm Si chips to keep the measurement area similar. ZEP is a modification of the PMMA polymer; hence, to understand the similarities of the new resists to ZEP, it was important to include PMMA into the study at this stage. As seen from the three spectra shown in Fig. 5, all of the resists have similar chemical structures.

Figure 6 shows the chemical structures of PMMA and ZEP. The methacrylate group is common in both the structures, with ZEP having two additional groups, i.e., the Cl-group and the phenyl group (β-methyl styrene). In Fig. 7(b), the peaks observed at 870 and 699 cm\(^{-1}\) are due to the phenyl rings and the Cl groups of ZEP, respectively. These peaks are missing in the PMMA spectra in Fig. 7(a). The doublet peaks at 1725 and 1750 cm\(^{-1}\) in the ZEP spectrum represent the C–O bond in the ester group. The shifting of the C–O peak to a higher wavenumber is seen when the Cl atom is closer to the carbonyl group.\(^{12}\)

When SML was compared with both resists, it was found to be more analogous to PMMA, except for the two intense peaks at 813 and 873 cm\(^{-1}\), corresponding to the aromatic rings. Nevertheless, a peak for the Cl groups was absent in SML, unlike ZEP. Moreover, in the SML, spectrum peaks at 1149 cm\(^{-1}\) suggest the presence of a C–O–C stretch from an ester group, alike to the other two resists. The peak at 1732 cm\(^{-1}\), a characteristic peak of PMMA resist,\(^ {13}\) was also seen in SML, representing the C=O stretch of the acrylate group. The peaks at 1388 and 750 cm\(^{-1}\) in the PMMA spectrum can be attributed to the χ-methyl vibrational groups, which are present in SML as well. Thus, it could be established from the three spectra that the SML resist has a backbone of methyl acrylate like the other two resists. However, SML does differ from PMMA with respect to the occurrence of the aromatic peak and from ZEP due to the absence of Cl group.

On comparing the contrast curves of the three resists in Fig. 1(a), it is seen that although SML has a similar contrast value \( (γ = 12) \) with respect to ZEP \( (γ = 11) \) and PMMA \( (γ = 12) \), its sensitivity is almost five times lower than that of ZEP and slightly lower than that of PMMA. The very high sensitivity of the ZEP resist has been associated with the presence of the Cl group in its polymer chain.\(^ {11,14}\) The e-beam sensitivity of polymethylstyrene is low, and it is understood that chlorine induces additional scattering events, which results in a scission in the main backbone of ZEP. Thus, due to the lack of such a scission-initiation group, SML demonstrates reduced sensitivity. On the other hand, while comparing with PMMA, the FTIR spectra suggest that SML has an additional methylstyrene group in the main polymer chain as compared to PMMA. Hence, the electron dose required to break the extra molecules in the SML polymer chain is higher than that for PMMA. These reasons could account for the reduced sensitivity of SML compared to ZEP and PMMA. Moreover, when ZEP and PMMA were compared, the higher etch resistance of ZEP observed was attributed to the χ-methylstyrene moiety.\(^ {15}\) As reported in our previous paper, the etch durability of SML is very similar to that of the ZEP resist\(^ {8}\) and can be attributed to the presence of the χ-methylstyrene group, as revealed by the FTIR analysis of SML, and its effect on the lithographic performance.

Figures 8(a) and 8(b) show the FTIR spectra of exposed and unexposed ZEP and SML, respectively. In Fig. 8(a), the most obvious difference noticed was the peak at 817 cm\(^{-1}\). The peak area also increased significantly after irradiation of the ZEP resist by e-beam. The IR peak in this region can be accredited to a >C=CC< stretch. This increase in the peak at 817 cm\(^{-1}\) suggests that there is an increase in unsaturation (C=C) within the polymer chain upon exposure. The major known chemical changes that occur after irradiation of any polymer is main chain-scission, formation of new bonds (C=C) and the evolution of gases such as CO\(_2\). Another
peak shown in Fig. 8(a) at 1230 cm$^{-1}$ reduced after e-beam exposure; this peak can be attributed to a C–O–C asymmetric stretch. The reduction in this peak suggests the breaking of C–O bonds in the acrylate group of ZEP. In the case of SML, similar results were observed. The most obvious peak enlargement that was observed in Fig. 8(b) was around 700–800 cm$^{-1}$, which also suggests an increase in unsaturation, i.e., formation of $\text{C}=$C$\equiv$ group by the breaking of the main polymer chain. A reduction in the peak at 1192 cm$^{-1}$ for exposed SML was also observed. This peak can be
attributed to an ester C–O stretch that is reduced after radiation, which indicated the dissociation of the acrylate group in the SML polymer chain. In a recent FTIR study of PMMA, to understand the reaction mechanism after e-beam irradiation, it was found that an increase in the C=CH bonds along with the increase in the e-beam dose led to the main chain scission of the PMMA polymer chains. Breaking of the carbonyl group in the polymer was also reported after e-beam radiation. Since the spectra in Fig. 5 suggest that all three resists have similar structures, the resists may undergo similar scission in the main chain during exposure. Moreover, increase in unsaturation is also observed in SML and ZEP resists along with the indications of in the reduction of carbonyl peak after irradiation of the resists. The course of the reaction for ZEP resist after irradiation is, however, reported to be different due to the presence of the Cl and phenyl groups. Similarly, SML may not have the same course of the main-chain scission as PMMA since a phenyl group is present in SML’s structure as well. Additionally, the SML polymer molecule may be larger (due to the additional groups present) than that of PMMA, which would take more electron dose to cleave the chain and hence the sensitivity observed is lower for SML.

IV. SUMMARY AND CONCLUSIONS

To summarize the study, we have demonstrated a link between the chemical properties of the SML and ZEP resists.
to their lithographic rendition. Roughness of SML and ZEP resists, along with incrementing e-beam doses, shows the effect of surface irregularity on the lithographic performance of the two resists. SML exhibits a lower surface roughness as a function of exposure dose when compared to ZEP, which is also reflected in the LER of the EBL patterned structures. Thus, the effect of initial surface roughness of a resist eventually determines the quality of the patterned lithographic structures.

Finally, the strong resemblance of the three FTIR spectra, SML, ZEP, and PMMA, confirms the analogous chemical composition of the three resist polymers. The lower sensitivity of SML as compared to ZEP can be attributed to the absence of a Cl group in the SML polymer, while the lower SML sensitivity in regard to PMMA is due to the presence of additional methylstyrene groups in SML. The good etch durability of SML can also be determined from the structural data acquired from the spectra and is due to the same –methylstyrene moiety, which is also present in ZEP but is absent in PMMA. A substantial amount of data could not be extracted from the FTIR spectra of irradiated resists; however, major changes such as an increase in unsaturation and alteration in acrylate groups in SML and ZEP were revealed.

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