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Mixture of ZEP and PMMA with varying ratios for tunable sensitivity as a lift-off resist with controllable undercut

Shuo Zheng, Ripon Kumar Dey, Ferhat Aydinoglu, and Bo Cui(✉)
Department of Electrical and Computer Engineering and Waterloo Institute for Nanotechnology (WIN), University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

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A lift-off process is a popular method to pattern metals, especially for the noble metals that are hard to dry-etch. For a “clean” lift-off process, an undercut profile is critical and is commonly achieved by using a bilayer resist stack. A resist with tunable sensitivity is apparently the most desirable, since it offers a controlled amount of undercut when used as the bottom layer, with the top layer being a less sensitive resist. In this study, the authors show that a simple mixture of poly (methyl methacrylate) (PMMA) and ZEP can offer tunable sensitivity by adjusting the ratio of the two resists dissolved in anisole. Higher sensitivity was attained by increasing the ZEP content in the mixture since ZEP is about 3× more sensitive than PMMA. However, the relationship is not a linear one, and the contrast curve for a mixture containing more PMMA (e.g., PMMA:ZEP ratio of 2:1) is closer to that of pure ZEP than to PMMA. For dense line array patterns with a periodicity of 200 and 500 nm, a moderate undercut obtained by using a low ZEP concentration (PMMA:ZEP = 2:1 as the bottom layer, PMMA as the top layer) gave the result for lift-off of 100 nm Cr. While using pure ZEP as the bottom layer, the undercut was too large that the resist lines collapsed because of capillary force or even completely detached when the adjacent undercut merged together. © 2016 American Vacuum Society. [http://dx.doi.org/10.1116/1.4967932]

I. INTRODUCTION

A lift-off process is a popular method to pattern metals, especially for the noble metals that are hard to dry-etch. In a lift-off process, a pattern is first defined in the resist using lithography. Then, a film of desired metal is blanket-deposited all over the substrate. Finally, the resist is dissolved, and the metal on top of it is thus lifted off, leaving behind metal structure that is originally in contact with the substrate. Yet when the material to lift-off is sensitive to solvent or liquid (e.g., organic conducting material), it is also possible to carry out a “dry lift-off” process without using any liquid.1 An undercut profile (i.e., opening is widest near the bottom) is always desirable in order to obtain a clean lift-off,2-5 because the undercut assures the metal on top of the resist is disconnected to that in contact with the substrate. If the undercut is large enough, a less directional deposition method such as sputtering can also be used for lift-off process, and the metal to lift-off can be very thick.

Various techniques have already been developed to attain an undercut profile. Slight undercut can be obtained using a single layer resist exposed by a low energy electron beam. For positive tone resist, single layer poly(methyl methacrylate) (PMMA) was reported to successfully create an undercut profile when exposed at a low energy of 3 keV that leads to more electron forward scattering than high energy exposure.6 For negative resists, lift-off is rarely used for pattern transfer because a slightly positively tapered profile, instead of an undercut profile, would usually result because of electron forward scattering. Nevertheless, lift-off using the negative resist such as polystyrene7 or water soluble poly(sodium 4-styrenesulfonate)8 can be realized when using very low energy exposure such that the resist bottom is inadequately exposed and thus dissolves fast in the developer. It is important to point out that, for lifting off some structures such as nanoscale trenches or holes, a negative resist is preferred as it offers far less exposure time than positive resists (yet a complicated double lift-off process using a positive resist can be employed to obtain such structures).2

A robust large undercut profile can be more readily achieved by using bilayer or trilayer (resist/hard mask/polymer) film stacks. For the case of bilayer, the bottom polymer could be either a resist having a different sensitivity than the top resist layer when developed using the same developer as the top layer or a different developer, or a non-resist that can be wet-etched using an etchant that will not attack the top resist layer. When both layers are positive e-beam resists, during exposure the proximate areas (that are not directly exposed) are exposed by the backscattered electrons, and such a proximity effect leads to a lateral extension of the structure. The extension is largely dependent on the exposure dose and sensitivity of the resist. When the exposure dose is fixed, the sensitivity difference between the two resists determines the amplitude of the lateral extension/undercut.

One of the most widely employed bilayer systems is a positive resist over a so-called lift-off resist polydimethylglutarimide (PMGI) or LOR (consists of mainly PMGI).10 PMGI is soluble in base solutions such as common developer for photolithography with greatly increased solubility upon electron beam exposure,11,12 but after being well baked it becomes insoluble to most acids and organic solvents, including common solvent developers for positive e-beam resists. The amplitude of undercut can be controlled by adjusting the soaking time in the base solution that dissolves PMGI without attacking the top organic resist layer.
However, wet chemical etching is generally not well reproducible and the amount of resulted undercut depends greatly on the opening in the top resist layer, with larger undercut for wider opening. Interestingly, it is found that solvent, particularly those used for developing PMMA including diluted methyl isobutyl ketone (MIBK), diluted methyl ethyl ketone and 2-ethoxyethanol (cellosolve), can also be used to develop PMGI with the sensitivity a few times lower than that of PMMA. As such, a double layer consisting of a PMGI top layer and a PMMA bottom layer can be used to attain a large undercut profile using the common developer for both resists.

In addition, a film stack of high molecular weight (Mw) PMMA/low Mw PMMA can provide a certain degree of undercut profile since the low Mw PMMA has higher sensitivity than the high Mw one. Yet for the chain scission resist, the dependence of sensitivity on Mw is very weak, because for longer chains, though more chain scission is needed to render it soluble in the developer, it also receives proportionally higher exposure dose. For instance, when Mw is decreased from 2200 to 50 kg/mol, PMMA’s sensitivity increases by only 26%. This weak dependence limits the achievable undercut. Alternatively, a copolymer of PMMA-co-PMAA [poly(methacrylic acid)] can be used as the under-layer as it is more sensitive than the top layer PMMA. ZEP can also be used as the bottom layer under PMMA as it is more sensitive than PMMA, but the undercut would be often too large since ZEP is ~3x more sensitive than PMMA. Alternatively, fullerene can be added into ZEP resist to make it less sensitive, and thus, a bilayer resist stack consisting of a fullerene-incorporated ZEP top layer and pure ZEP bottom layer can offer a large undercut profile. For the ZEP resist (as the top layer), besides LOR, PMMA has also been employed as a bottom layer that is more sensitive than ZEP when using undiluted MIBK as developer. Lastly, hydrogen silsesquioxane (HSQ) over PMMA has been employed successfully for lift-off, with the undercut profile created by excessive lateral etching of PMMA by oxygen plasma with the exposed HSQ (becomes effectively SiOx) as hard mask.

For the bottom layer, a resist with tunable sensitivity is apparently the most desirable, as it can offer a controlled amount of undercut. Ideally, a large undercut profile is preferred to enable the lift-off of very thick metals. But too large undercut may lead to the collapse of the top resist layer onto the substrate, and the situation gets worse for dense structures. With tunable sensitivity, the amount of undercut can be adjusted according to different applications in order to achieve an optimal lift-off process.

In principle, since the sensitivity (μC/cm²) for negative resists like polystyrene is inversely proportional to its number averaged molecular weight (Mn), one can achieve an undercut profile using a bilayer with the bottom layer having a lower molecular weight than the top one, and the relative sensitivity thus the amount of undercut can be tuned readily by choosing the appropriate Mn of the two layers. Though the exposed polystyrene becomes insoluble in common solvent because of the chain cross-linking, a hot mixture of NH_4OH, H_2O_2, and H_2O (RCA-1) can be used to dissolve it for lift-off. Unfortunately, despite our great effort, we were not able to find a solvent that can dissolve polystyrene for spin-coating without dissolving significantly the bottom polystyrene layer during spin-coating of the top layer. This is contrary to positive resists like PMMA and ZEP, which does not dissolve significantly (less than ~30 nm if the bottom resist layer is well baked, and the dispersion and spin-coating of the top resist is carried out quickly within 1 min).

In this study, we will show that a simple mixture of PMMA and ZEP can offer tunable sensitivity by adjusting the volume ratio of the two resists both dissolved in anisole. The mixture can be used as the bottom layer under PMMA, in order to obtain a controlled undercut profile for easy lift-off. Besides lift-off that is the subject of the present study, such a resist mixture having adjustable sensitivity can also be utilized to fabricate complicated quasi-3D structures mimicking Morpho butterfly scales using many layer resist film stacks, or an imprint mold for a dual damascene process to fabricate Cu interconnect for integrated circuit.

II. EXPERIMENT

PMMA (996 kg/mol) and CSAR-62 (a low-cost replacement of ZEP resist from AllResist Inc., and hereafter we still refer it as ZEP resist) were mixed together. As we do not have dry ZEP resist (as-purchased resist is already dissolved in anisole), we cannot mix dry ZEP with PMMA powder at a given weight ratio. Instead, we prepared PMMA solution in the anisole at a certain concentration such that it gave the same thickness as ZEP under the same spin-coating condition, and we assume this PMMA solution has the same weight concentration as the as-purchased ZEP. Then, we mixed this PMMA and ZEP solution at various volume ratios (PMMA: ZEP = 0:1, 1:2, 1:1, 2:1, and 1:0). For spin-coating the bilayer film, we first coated the mixture resist, followed by baking at 120°C for 10 min to drive off the solvent. Baking at a higher temperature and/or for a longer time might lead to undesirable phase-separation of PMMA and ZEP. Then, we quickly coated the PMMA on top of the mixture film and baked it at 120°C for very short time to minimize intermixing between the two layers. During spin-coating the top layer, the bottom layer was dissolved by ~30 nm that is acceptable since each layer was close to 250 nm thick.

Next, the bilayer resist was exposed using LEO 1530 SEM equipped with NPFS pattern generation system at 20 keV and 0.8–5 nC/cm line dose. After the exposure, the resists were developed in amyl acetate, a common e-beam developer for ZEP, yet also a good developer for PMMA, for 1 min. Finally, 100 nm Cr was evaporated and then lifted off by dipping the samples into the anisole for about 10 min, followed by ultrasonic agitation for 15 s in the same anisole solution.

III. RESULTS AND DISCUSSION

A. Resist contrast curves

In order to confirm our assumption that the mixture resist’s sensitivity can be tuned by adjusting the ratio of the...
two resist components, we first measured the mixture resist’s contrast curves using AFM, which is plotted in Fig. 1, together with the contrast curves for the pure ZEP and pure PMMA resist under the same development condition. For the contrast curves measurement, a single layer of pure or mixture resist was spin-coated with thicknesses of approximately 250 nm. As expected, higher PMMA/ZEP ratio leads to lower sensitivity (higher clearance dose). The clearance dose for pure ZEP resist exposed at 20 keV is 42 μC/cm² with a contrast of ~7. The sensitivity is close to typical values reported in the literature. But for pure PMMA, it is considerably more sensitive with a clearance dose of approximately 61 μC/cm² than typical values (~200 μC/cm²) obtained using the common MIBK:isopropyl alcohol = 1:3 developer, suggesting that amyl acetate is a stronger solvent developer than diluted MIBK.

However, the resist’s property is apparently dominated by the more sensitive resist (here ZEP) in the mixture. For instance, the mixture of PMMA:ZEP = 2:1 has a contrast curve closer to that of pure ZEP resist than to pure PMMA even though it contains more PMMA. This property can be explained by the fact that PMMA molecular chains are not entangled with other PMMA chains and attached to a solid substrate; instead, it is embedded in the ZEP matrix. And thus once ZEP becomes soluble in the developer, the PMMA (though still with long chain) will be “lifted off” and effectively dissolved in the developer. This result implies that one has to use a mixture with a very high PMMA/ZEP ratio in order to achieve a contrast curve lying near the middle of the two contrast curves for the two pure resists. For instance, the contrast curve for the 5:1 ratio lies near the middle of the two contrast curves for the two pure resists, though at lower doses it is closer to the contrast curve of pure PMMA because, at such low doses, the ZEP is not very soluble and the PMMA dominates the development process because of its much higher concentration in the mixture. Nevertheless, for our purpose, the lateral undercut is determined by the portion of the contrast curves with low exposure dose by backscattered electrons (e.g., a dose of ~35 μC/cm² in the contrast curves), rather than the dose at clearance. As seen, at such low exposure doses, the amount of resist developed depends significantly on the ratio of the two resists in the mixture; and thus the amplitude of undercut in the bilayer resist system can be adjusted effectively by using different ratios without the need for very high PMMA/ZEP ratio.

B. Resist profile and lift-off of thick Cr

Undercut profile is greatly desired for a clean lift-off process. In order to verify the correlation between the resist sensitivity for the bottom layer and the amplitude of undercut, we exposed the bilayer resist with periodic line-array structures. The top layer was pure PMMA, and the bottom layer was the mixture of PMMA and ZEP or pure ZEP resist. The lines were exposed with single pass line pattern with varying line doses (unit nC/cm). Because of electron forward scattering and backscattering, the line-width increases with line dose and can go far beyond the electron beam spot size. Figure 2 shows the resist profile after development in amyl acetate. Figures 2(a) and 2(b) are structures with a line array periodicity of only 200 nm exposed at a line dose of 1.32 nC/cm at 20 keV, with the bottom layer, respectively, of PMMA: ZEP = 2:1 and pure ZEP. This dose is determined as the optimal dose as it is high enough to expose the top (less sensitive) PMMA layer, and at the same time gives a reasonably large undercut without resist structure detachment when using PMMA: ZEP = 2:1 as the bottom layer. The undercut profile is evident for the mixture resist bottom layer, with some lines collapsed because of capillary force that becomes significant when the resist structure height is larger than its width. However, when the bottom layer is pure ZEP that has higher sensitivity than the mixture resist, the lines were all detached because the undercut was so large that they nearly merged together.

Figures 2(c)–2(f) are line arrays with a larger array periodicity of 500 nm, all exposed with an optimal line dose of 1.77 nC/cm at 20 keV. The dose is higher than the optimal dose for 200 nm array periodicity (1.32 nC/cm) because of lower pattern density and thus less contribution from proximity exposure. Again, the top layer is PMMA, and the bottom layer is, respectively, a PMMA:ZEP ratio of 2:1, 1:1, 1:2, and 0:1 (pure ZEP). Clearly, the amplitude of the undercut increased with the amount of ZEP in the mixture. For a PMMA:ZEP ratio of 2:1 and 1:1, the amount of undercut was very close (70 and 75 nm, respectively), since their contrast curves nearly overlapped at a low dose region of ~40 μC/cm² as shown in Fig. 1. The undercut increased quickly to 104 nm for the 1:2 ratio mixture. When pure ZEP was used as the bottom layer, most resist lines were detached because of too high or even merged undercut.

For lift-off study, 100 nm Cr, which is pretty thick for lift-off, was deposited by electron beam evaporation on the resist structure with 500 nm array periodicity, and then lifted off in anisole. Figure 3 shows the resulted Cr line array structures. As expected, best lift-off result was obtained for the PMMA:ZEP = 2:1 ratio [Fig. 3(a)]. For the resist mixture with higher ZEP content [Figs. 3(b)–3(d)] and thus higher

![Fig. 1. (Color online) Contrast curves for the PMMA-ZEP mixture resist, as well as for pure PMMA and ZEP resist. The resists were exposed at 20 keV and developed in amyl acetate for 1 min. The ratios in the graph were volume ratios of PMMA:ZEP.](image-url)
sensitivity and larger undercut, either very wide Cr lines because of merged adjacent lines caused by too large undercut, distorted Cr lines, and/or unsuccessful lift-off (Cr on top of PMMA is not lifted off because of the resist structure falling down when the undercut is too large), are evident.

IV. CONCLUSIONS

We studied the exposure property of the PMMA:ZEP mixture resist. The mixture behaved like the typical positive resist without noticeable microphase separation. The resist sensitivity increases with the content of ZEP in the mixture.
since ZEP is much more sensitive than PMMA; and the contrast curve of the mixture resist is closer to that of ZEP than to PMMA even with a PMMA:ZEP ratio of 2:1. With tunable sensitivity, the mixture resist is ideal for lift-off when used as the bottom layer, with the top layer being PMMA. The amplitude of undercut for such a bilayer resist was adjusted readily by choosing different PMMA:ZEP ratios. However, though large undercut is desired for lift-off, too large undercut made the resist lines susceptible to collapse because of capillary force. With even larger undercut (by using pure ZEP as the bottom layer), the undercut of adjacent line structures merged together for 200–500 nm period line arrays, and the resist lines were thus completely detached after development. A moderate undercut obtained using PMMA:ZEP = 2:1 as the bottom layer gave a well-defined resist line structure with array periodicity of 200 or 500 nm. This moderate undercut also resulted in the best result for the lift-off of 100 nm Cr. Larger undercut would be more suitable for larger (well beyond 500 nm) array periodicity.

Our technique has two main advantages. First, PMMA and ZEP are kinds of the two must-have resists in most labs particularly with the recent introduction of low-cost ZEP replacement from various suppliers. Second, our technique is more reliable than using PMGI or LOR as the bottom layer, as the latter requires precise control of the wet etching time for dissolving the bottom layer.