Metal and organic nanostructure fabrication by electron beam lithography and dry liftoff

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Abstract— **Liftoff and direct etch are the two most popular pattern transfer methods used for nanofabrication. The latter is limited by the etching rate selectivity between the resist and the substrate material, which is usually on the order of unity for dry plasma etching. Moreover, some metals including most noble metals cannot be dry etched. Thus liftoff is often the preferred pattern transfer method. Liftoff is typically carried out using a solvent that dissolves the resist. A strong solvent aided by ultrasonic agitation and/or heating is sometimes needed if the resist is difficult to dissolve due to, for example, cross-linking by exposure to electron beam or plasma. Another serious issue with conventional liftoff process is that the metal debris may stay at the active device area after drying. To avoid the above issues, dry liftoff using mechanical approach may be utilized. Here we report a simple dry liftoff technique using a scotch tape to peel off the resist film coated with the material to lift off. We obtained high resolution (down to 50 nm) liftoff of metal and organic materials polystyrene and Alq3, with PMMA as electron beam resist coated on a substrate treated with a low energy surfactant.**

I. INTRODUCTION

Direct etch and liftoff are the two most popular pattern transfer processes. In the direct etch process, the polymer resist is first patterned using a lithography technique such as electron beam lithography (EBL), then the pattern is transferred to the substrate or sub-layer with the resist as mask by a dry etching technique such as reactive ion etching. In the liftoff process, the film (commonly metal) is coated on the resist structure, and the film on top of resist structure is lifted off when the resist underneath is dissolved, leaving behind the film structure on the area previously uncovered by resist. Compared to direct etch, liftoff is more versatile since it can work for most metals, whereas many metals including most noble metals cannot be etched by dry etching.

However, for liftoff the solvent or aqueous solution that dissolves the resist must not attack the substrate or the material to liftoff, which can be a conducting polymer for some applications. As a result, solvent-free liftoff or dry liftoff process is desirable. In dry liftoff, the patterned resist coated with the film is peeled off the substrate using a scotch tape, rather than dissolved by a solvent. As such, our dry liftoff process resembles stencil lithography[1], which duplicates the pattern on the stencil (shadow) mask by evaporation of the desired material through the stencil mask onto the substrate. Compared to dry liftoff, stencil lithography suffers from a few drawbacks.

First and the most serious, the gap between the mask and the substrate is difficult to control, leading to blurring (an enlargement of the initial pattern)[2], whereas in dry liftoff the "shadow mask" (resist pattern) is in contact with the substrate with zero gap. Another source of blurring with non-zero gap is the adatom diffusion. In stencil lithography, the gap is caused not only by the non-flat wafer surface (typical wafer has total thickness variation (TTV) of several micrometers), but also caused by the stress of the deposited film on the silicon nitride membrane that is the most popular stencil mask material. To minimize the effect of stress, the membrane has to be corrugated that further complicates the stencil mask fabrication process[3]. Alternatively, zero gap can be obtained using a stencil mask made of a soft material polydimethylsiloxane (PDMS) that forms conformal contact even with curved substrate. However, to make the PDMS membrane mechanically strong enough, its thickness needs to be at least 10 μm that limits the resolution to micro-scale (for comparison, the thickness of Si_3N_4 membrane supported by bulk silicon can be down to 10 nm) [4]. The second drawback for stencil lithography is the clogging of the aperture on the stencil mask by the deposited material that has to be removed regularly, though the clogging can be reduced by coating the stencil mask with a self-assembled monolayer having low surface energy[5]. Nevertheless, stencil lithography is obviously superior to our process in that the stencil mask can be re-used multiple times and is thus viable for scaled up production, whereas in dry liftoff the resist has to be patterned by a lithography process every time.

In this paper, we will present dry liftoff of metal (Cr), as well as of organic conducting material tris-(8-hydroxy quinoline) aluminum (Alq3, a common component of organic light-emitting diodes) with resolution down to 50 nm. Previously, various techniques have been demonstrated to pattern organic conducting materials. Firstly, one can obviously use an "orthogonal" solvent such as hydrofluoroether that does not dissolve or adversely damage the organic layer[6]. Yet, on the other hand, the solvent must be able to dissolve the resist pattern for liftoff. As a result, the choice of the solvent and the corresponding resist is rather limited, with one example as Teflon-AF being the nanoimprint resist and FC-40 (completely fluorinated aliphatic compound) being the solvent[7]. Secondly, thermal nanoimprint lithography or hot embossing is also a dry process able to structure a conducting polymer[8], but the structures are all connected by a thin residual layer. One

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method that resulted in zero residual layer is to use a mold consisting of ultra-sharp structures to locally "rupture" the film having residual stress, which was reported to pattern poly(3-hexylthiophene) (P3HT) at moderate pressure of 5 bar and temperature of 100°C [9]. Thirdly, a couple of organic conducting materials, including poly(3-octylthiophene) (P3OT) [10] and poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) [11,12], are electron beam resist and can thus be patterned directly by electron beam lithography. Fourthly, some conducting polymers can be rendered photo-sensitive (thus patternable by photolithography) by attaching side groups to the polymer backbone and mixing with photoacid generators [13], whereas some others can be synthesized from precursor film into microstructure by photolithography or scanning near-field optical lithography[14]. Fifthly, crystallization from vapor phase of some organic semiconducting materials such as pentacene can be confined onto chemical patterns generated by micro-contact printing[15].

Compared to the above methods, our dry liftoff approach is relatively straightforward and can pattern most organic (conducting) materials that can be deposited by thermal evaporation. More importantly, our technique offers a much higher resolution when using a high resolution electron beam resist such as poly(methyl methacrylate) (PMMA). However, one major limit of dry liftoff is the incapability of obtaining arbitrary patterns such as a ring or mesh structure because the isolated resist structure inside the ring or mesh would be difficult to peel off using a scotch tape.

II. EXPERIMENT

Among the electron beam resists we worked with, we found that polycarbonate resist has the poorest adhesion to the bare silicon substrate. In fact, we have had difficulty to achieve a strong adhesion needed for development using hot NaOH aqueous solution as developer, which had motivated us to find solvent developers[16]. This weak adhesion encouraged us to try polycarbonate resist first for dry liftoff. We dissolved 60 kg/mol bisphenol A polycarbonate in cyclopentanone to make a 4 wt/vol% solution that gave a 200 nm uniform film by spin-coating on a silicon wafer. The film was then baked on a hotplate at 120°C for 5 min. After exposure at 20 keV using Raith150^{TWO} electron beam lithography system, the resist was developed in a 1:3 mixture of cyclopentanone and 2-propanol for 30 sec at room temperature followed by rinsing using 2-propanol. Finally we coated 10 nm Cr and peeled off the resist film using a scotch tape.

Next, to achieve high resolution dry liftoff, we studied PMMA that is the most popular high resolution e-beam resist. As PMMA has strong adhesion to the silicon substrate due to its relatively high surface energy, surface treatment of the substrate is indispensible. We thus treated the silicon wafer with low surface energy self-assembled monolayer (SAM) of perfluorooctyltrichlorosilane (FOTS, Sigma-Aldrich Co.) that is commonly used as an anti-adhesion layer for nanoimprint lithography. However, the normal procedure using vapor-phase treatment under vacuum for several hours led to a surface energy too low for spin coating (resist solution formed beads and fell off the wafer). Therefore, we simplified the process and placed the wafer piece and a drop of FOTS inside a wafer box (without vacuum), and reduced the treatment time to 30 min so that the resulted surface energy was suitable for both peeling-off and spin coating of PMMA dissolved in a non-polar solvent toluene. We used 996 kg/mol PMMA and 3 wt/vol% concentration, which gave a 560 nm-thick film that was subsequently baked on a hotplate at 120°C for 10 min. Here we cannot use the more popular solvent for PMMA for spin coating, notably anisole and chlorobenzene, since they are both polar and thus do not wet the silicon substrate coated with the anti-adhesion SAM layer. Alternatively, for substrates incompatible with such an anti-adhesion treatment, a low surface energy thin fluorocarbon film can be coated using CHF3, C4F8, or CF4/H2 plasma[17]. After exposure at 20 keV, the resist was developed in 2-propanol (IPA) : H_2O =7:3 or methyl isobutyl ketone (MIBK) : IPA = 1:3, both for 1 min. Finally, metal or organic film was coated respectively by electron beam or thermal evaporation, followed by dry liftoff using a scotch tape to peel off the film-coated resist structure.

It is also desirable to study dry liftoff using ZEP resist that is widely utilized with about three times higher sensitive than PMMA. However, the as-purchased ZEP is dissolved in anisole that cannot be spin-coated on FOTS-treated silicon wafer. On the other hand, ZEP has weaker adhesion to the substrate than PMMA due to its lower surface energy (yet ZEP film cannot be peeled off from un-treated silicon substrate). Thus we selected a less hydrophobic silane surfactant, trichloro (phenyl) silane (Gelest Inc.), which was found to give the proper surface energy for dry liftoff (that is, ZEP dissolved in anisole can be spin-coated on the substrate and peeled off at a later step).

III. RESULTS AND DISCUSSION

Here we have chosen electron beam lithography to pattern the resist for subsequent dry liftoff. In principle other lithography techniques, such as nanoimprint lithography, can also be employed to pattern the resist for dry liftoff. However, since the adhesion between the resist and the substrate must be weak enough for dry liftoff, resist peeling off during demolding could be a serious issue for nanoimprint lithography. In addition, the resist profile would be positively tapered (wider opening at resist top than bottom) after plasma etching the residual layer, making a clean liftoff challenging particularly for high resolution structures. Alternatively, a polymer film (not a resist) may be structured by lithography and pattern transfer with the resist atop as etching mask; and some films such as parylene have poor adhesion to the substrate (and are resistant to common solvents used to dissolve the resist for spin-coating on top of parylene), and are thus suitable for dry liftoff [18,19,20]. However, again, sub-micron resolution is difficult to achieve because the pattern profile in parylene is positively tapered due to lateral etching in the pattern transfer step.

Figure 1 shows the dry liftoff process and the liftoff of 10 nm Cr using polycarbonate electron beam resist. As seen, Cr could be dry lifted off, but the pattern was not "clean" with very rough edges. This is probably because of the positively tapered profile of the polycarbonate resist pattern, which is in turn due to the low contrast of polycarbonate resist and the fact that the resist at the upper part was developed for longer time and thus was wider than the lower part. A positively tapered profile resulted in coating on the sidewall and hence a connected metal film across the pattern edge; and during the peeling off process, the metal film was broken near the pattern edge, leading to rough edges.

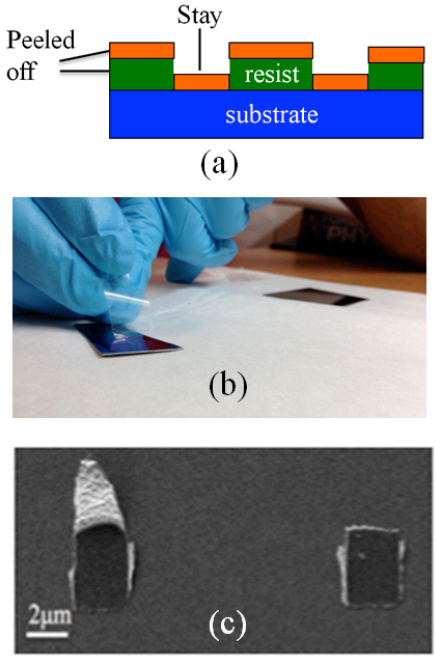

Figure 1. Schematic (a) and photograph (b) showing the peeling off (dry liftoff) process using a scotch tape. (c) SEM image of Cr microstructure fabricated by dry liftoff using polycarbonate as electron beam resist.

Figure 2a shows SEM image of Cr line array pattern after dry liftoff using 560 nm-thick PMMA resist, with resolution down to ~50 nm. Higher resolution is possible by using thinner PMMA resist. Here a clean liftoff is possible because PMMA has a high contrast that leads to a slightly undercut profile (narrower opening at resist top than bottom) due to electron forward scattering. With high contrast, the resist profile is mainly determined by electron energy deposition, and the longer development time at the upper part of the resist structure does not significantly widen the opening. Figure 2b shows the dry liftoff of large Cr squares exposed at different doses. For over-exposed large square patterns at the upper right, peeling off was not obtained, which is because PMMA becomes negative resist at very high doses and the cross-linked PMMA adheres strongly to the FOTS-treated substrate. Moreover, at such high doses FOTS may be seriously degraded by electron beam exposure thus losing its anti-adhesion property[21]. The squares also became larger (than the designed pattern) and more rounded at higher doses, which is because of exposure by backscattered electrons (i.e. proximity effect) that becomes significant when the dose is high.

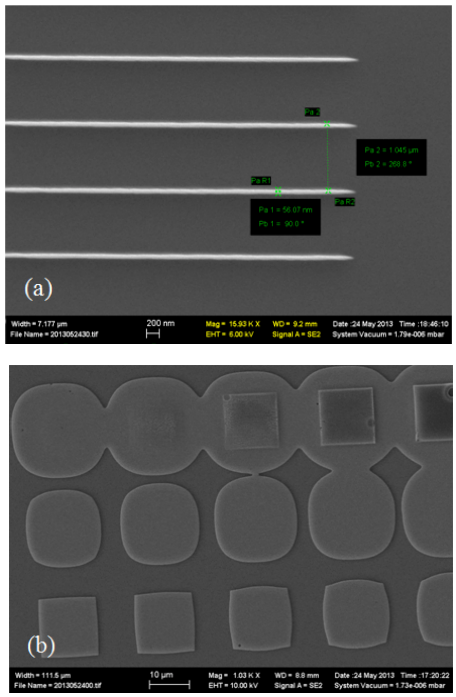

Figure 2. SEM images of Cr patterns after dry liftoff of 10 nm Cr. Here the substrate Si was etched by RIE in order to obtain higher image contrast. (a) Line array with 55 nm line-width; (b) Large squares having doses increasing exponentially from lower left to upper right. At very high doses, PMMA becomes a negative resist and the cross-linked area (the three squares at upper right) was not peeled off.

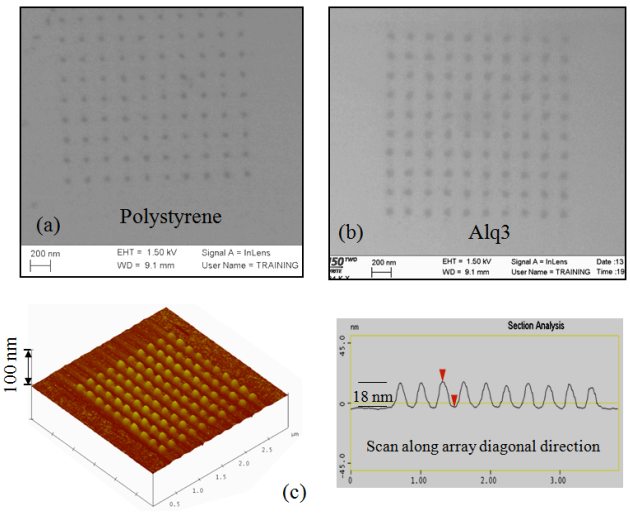

Figure 3. SEM images of dry lifted off 15 nm-thick polystyrene (a) and 18 nm-thick Alq3 (b), with array period of 200 nm and dot diameter of ~50 nm. (c) AFM image of Alq3 dot array with 200 nm period.

Lastly, since the pattern transfer process is a dry process, it can be utilized to lift off organic materials that may be susceptible to the solvent used for normal (wet) liftoff process. Figure 3 shows dot array of polystyrene (that is actually also an electron beam resist[22,23,24] and can be evaporated when its molecular weight is low, here 1.2

kg/mol [25,26]), and dot array of Alq3 (a popular organic conducting material), which were both deposited by thermal evaporation with thickness of 15 nm and 18 nm, respectively. Very high resolution down to 50 nm was achieved, indicating clearly the superior capability of the dry liftoff process as compared to other techniques reported to pattern organic conducing materials.

IV. CONCLUSION

Here we explored the potential of a dry liftoff process to pattern metals as well as organic materials using electron beam lithography. The liftoff was realized by mechanically peeling off the resist film coated with the material to lift off, rather than dissolving the resist using a solvent as is the case for conventional (wet) liftoff process. To facilitate the peeling off, the resist's adhesion to the substrate must be weak, which is the case for polycarbonate electron beam resist. But we were not able to obtain sub-micron dry liftoff using polycarbonate resist, presumably because of its low contrast. Otherwise, the substrate has to be treated with a low surface energy surfactant. However, too low surface energy makes resist spin-coating on the substrate impossible due to dewetting. For PMMA resist, we optimized the substrate surface treatment process, and obtained high resolution ~50 nm Cr pattern by dry liftoff. The same process was also employed to pattern polystyrene and an organic conducting material Alq3 (both can be deposited by thermal evaporation) with similar resolution.

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REFERENCES

[1] O. Vazquez-Mena, G. Villanueva, V. Savu, K. Sidler, M. A. F. van den Boogaart and J. Brugger, "Metallic nanowires by full wafer stencil lithography", Nano Lett., 8, 3675-3682 (2008).

[2] O. Vazquez-Mena, L. G. Villanueva, V. Savu, K. Sidler, P. Langlet and J. Brugger, "Analysis of the blurring in stencil lithography", Nanotechnol., 20, 415303 (2009).

[3] M. Lishchynska, L. M. Doeswijk, J. C. Greer and J. Brugger, "Corrugated membranes for improved pattern definition with micro/nanostencil lithography", Sensor Actuator A-Phys , 130, 568-574 (2006).

[4] R. J. Jackman, D. C. Duffy, O. Cherniavskaya and G. M. Whitesides, "Using elastomeric membranes as dry resists and for dry liftoff", Langmuir, 15, 2973–2984 (1999).

[5] X. M. Yan, A. M. Contreras, M. M. Koebel, J. A. Liddle and G. A. Somorjai, "Parallel fabrication of sub-50-nm uniformly sized nanoparticles by deposition through a patterned silicon nitride nanostencil", Nano Lett. 5, 1129-1134 (2005).

[6] A. A. Zakhidov, J. K. Lee, H. H. Fong, J. A. DeFranco, M. Chatzichristidi, P. G. Taylor, C. K. Ober and G. G. Malliaras, "Hydrofluoroethers as orthogonal solvents for the chemical processing of organic electronic materials", Adv. Mater., 20, 3481-3484 (2008).

[7] Y. C. Lo, D. W. Li, Z. Sun and S. Shaik and X. Cheng, "High-resolution nanodestructive patterning of isolated organic semiconductors", J. Vac. Sci. Technol. B, 30, 06FB04 (2012).

[8] L. J. Guo, "Nanoimprint Lithography: Methods and Material Requirements", Adv. Mater., 19, 495-513 (2007).

[9] X. He, J. Winkel and W. T. S. Huck, "Nanopatterning via pressure-induced instabilities in thin polymer films", Adv. Mater., 21, 2083-2087 (2009).

[10] S. X. Cai, M. Kanskar, J. C. Nabity, J. F. W. Keana and M. N. Wybourne, "Fabrication of submicron conducting and chemically functionalized structures from poly(3-octylthiophene) by an electron beam", J. Vac. Sci. Technol. B, 10, 2589-2592 (1992).

[11] J. G. Park, G. T. Kim, J. H. Park, H. Y. Yu, G. McIntosh, V. Krstic, S. H. Jhang, B. Kim, S. H. Lee, S. W. Lee, M. Burghard, S. Roth and Y. W. Park, "Quantum transport in low-dimensional organic nanostructures", Thin Solid Films, 393, 161-167 (2001).

[12] R. Stabile, A. Camposeo, L. Persano, S. Tavazzi, R. Cingolani and D. Pisignano, "Organic-based distributed feedback lasers by direct electron-beam lithography on conjugated polymers", Appl. Phys. Lett., 91, 101110 (2007).

[13] M. C. Gather, A. Köhnen, A. Falcou, H. Becker and K. Meerholz "Solution-processed full-color polymer organic light-emitting diode displays fabricated by direct photolithography", Adv. Funct. Mater, 17, 191-200 (2007).

[14] F. Cacialli, R. Riehn, A. Downes, G. Latini, A. Charas and J. Morgado, "Fabrication of conjugated polymers nanostructures via direct near-field optical lithography", Ultramicroscopy, 100, 449-455 (2004).

[15] A. L. Briseno, S. C. B. Mannsfeld, M. M. Ling, S. Liu, R. J. Tseng, C. Reese, Mark E. Roberts, Y. Yang, F. Wudl and Z. Bao, "Patterning organic single-crystal transistor arrays", Nature 444, 913-917 (2006).

[16] A. S. Abbas, M. Yavuz and B. Cui, "Polycarbonate electron beam resist using solvent developer", Microelectron. Eng., 113**,** 140 –142 (2014).

[17] R. Muhammad, S. H. Cho, J. H. Lee and J. G. Park, "Fluorocarbon film-assisted fabricationof a CoNi mold with high aspect ratio for nanoimprint lithography", Microelectron. Eng., 104, 58-63 (2013).

[18] S. Takeuchi, D. Ziegler, Y. Yoshida, M. Mabuchi and T. Suzuki, "Parylene flexible neural probes integrated with microfluidic channels", Lab Chip, 5, 519-523 (2005).

[19] B. Ilic and H. G. Craighead, "Topographical patterning of chemically sensitive biological materials using a polymer-based dry lift off", Biomedical Micriodevices, 2, 317-322 (2000).

[20] J. A. DeFranco, B. S. Schmidt, M. Lipson and G. G. Malliaras, "Photolithographic patterning of organic electronic materials", Organic Electronics, 7, 22-28 (2006).

[21] A. Alshammari, C. Con, M. Yavuz and B. Cui, "Benchtop fabrication method on non-planar surface using SAM as e-beam resist", 58th International Conference on Electron, Ion and Photon Beam Technology and Nano-fabrication (EIPBN), Washington, DC, May 2014.

[22] S. Ma, C. Con, M. Yavuz and B. Cui, "Polystyrene negative resist for high resolution electron beam lithography", Nanoscale Research Letters, 6, 446 (2011).

[23] C. Con, R. K. Dey, M. Ferguson, J. Zhang, R. Mansour, M. Yavuz and B. Cui, "High molecular weight polystyrene as very sensitive electron beam resist", Microelectronic Engineering, 98, 254-257(2012).

[24] R. K. Dey and B. Cui, "Effect of molecular weight distribution on e-beam exposure properties of polystyrene", Nanotechnol., 24, 245302 (2013).

[25] J. Zhang, C. Con and B. Cui, "Electron beam lithography on irregular surfaces with evaporated resist", ACS Nano, 8, 3483–3489 (2014).

[26] C. Con, J. Zhang and B. Cui, "Nanofabrication of high aspect ratio structures using evaporated resist containing metal", Nanotechnol., 25, 175301 (2014).