Electron Beam Lithography on Irregular Surface Using Grafted PMMA Monolayer as Resist

Ripon Kumar Dey, Ferhat Aydinoglu, and Bo Cui*

1. Introduction

A common challenge in nanofabrication is to fabricate nanostructures on irregular surfaces, which has application in many areas including optical devices,[5] MEMS (Micro-Electro-Mechanical-System),[2] super-adhesive devices,[3] and electronic devices.[4] More specifically, tip-enhanced Raman spectroscopy (TERS)[5] which is used for chemical analysis and lab-on-fiber cantilevers, and then the patterns are transferred to the layer underneath. A high resolution of 30 nm line width is achieved using this monolayer resist. Nanofabrication on irregular surfaces may have applications in the fields of tip-enhanced Raman spectroscopy for chemical analysis and lab-on-fiber technology for sensor applications.

An electron beam resist is usually coated by conventional coating methods such as spin-coating, which cannot be reliably applied on irregular surfaces. Therefore, there is still a great demand for an easier process where a cheap and readily available resist can be coated on non-flat surface for patterning nanostructures with high resolution. Here, it is demonstrated that a monolayer resist can be grafted on non-flat surface to enable nanofabrication on it. As a proof-of-concept of patterning on irregular surfaces, poly(methyl methacrylate) (contains 1.6% methacrylic acid that has the carboxyl group needed for grafting) is chosen and is grafted on irregular surfaces by thermal treatment which induces a chemical reaction of the carboxyl group with the hydroxyl group on substrate. Subsequently, nanostructures are patterned by electron beam lithography on this monolayer resist grafted on non-flat surface such as atomic force microscopy (AFM) cantilevers, and then the patterns are transferred to the layer underneath.

To pattern on nonplanar surfaces is more challenging than on flat surfaces. This is because conventional coating methods, such as spin-coating method which is very popular in nanofabrication technique, cannot be reliably applied to coat uniform electron beam resists on nonflat surfaces. Unlike spin-coating technique, spray coating method,[14] and Langmuir–Blodgett (LB) technique[15] may be employed to coat resist on non-planar surfaces, but they have several limitations including sample should be free from sharp corners or edges for spray coating, and very few materials are usable as e-beam resist for LB technique. Self-assembled monolayer (SAM) resist[16] can also be applied in patterning on nonflat surfaces. To do pattern transfer after self-assembly process, typically an intermediary wet etching technique is performed (dry etch is not suitable since self-assembled monolayer is too thin). However, wet etching using SAM resist mask has poor critical dimension control compared to dry etching[17] and those resists suffer from very low sensitivity. In addition, several nanolithography methods, such as focused ion beam lithography, can also be employed to pattern on irregular, nearly arbitrary surface; but it is more expensive than other conventional nanopatterning methods and its throughput is much lower than electron beam lithography (EBL). King et al.[18] and Gardener et al.[19] introduced a new type of patterning process called ice lithography where water vapor is introduced into the specimen cooled to <120 K. The thin ice film was patterned by electron beam exposure at low energy. However, there are two major drawbacks for ice lithography: the resist should be kept at very low temperature until pattern transfer is completed, and the resist sensitivity is very low compared to conventional resists (e.g., three orders lower than poly(methyl methacrylate), PMMA). Like ice resist, frozen CO2 can also be used as an electron-beam resist. But it has similar drawbacks that include low temperature requirement and low sensitivity.[20] A few resists including polystyrene[21,22] and silicon dioxide[21] can be deposited by thermal/e-beam evaporation technique on non-flat surface. However, they still suffer from very low sensitivity, and vacuum deposition techniques are expensive compared to spin-coating. In addition, there are only a few resists that can be evaporated. A self-developing resist such as AlF3, which can be evaporated on irregular surfaces, is also an extremely insensitive resist.

DOI: 10.1002/admi.201600780
reliably on nonflat surface such as on an AFM cantilever, and can be used for patterning nanostructure using electron beam lithography. In this process, the PMMA is grafted onto a surface terminated with hydroxyl group in a way similar to forming the polystyrene-r-PMMA copolymer,[25,26] brush that is widely used to provide a neutral surface for block copolymer self-assembly.

Our process offers a range of advantages. The PMMA monolayer is thicker by about one order than self-assembled monolayer resist, thus easier for pattern transfer. In addition, it is a low cost process, as it employs only spin- or dip-coating method. Moreover, since it is a thin film firmly bonded to the sublayer/substrate, the monolayer can eliminate pattern collapse due to the capillary force when using liquid development, which is a serious concern for spin-coated (thick) resists. Another advantage for a polymer monolayer coating method over spin-coating is the lack of edge-bead effect, which is also a serious problem for spin-coating.[27] It is thus suitable for patterning on ultrasmall substrate without having any edge-bead effect. Last, besides acting as a monolayer e-beam resist that is terminating ultrasmall substrate without having any edge-bead effect, it is a good solvent thus cannot be utilized as a developer, here MIBK:IPA can be used as developer for the monolayer resist, thus easier for pattern transfer. In addition, since it is a thin film firmly bonded to the substrate, it is a low cost process, as it employs only spin- or dip-coating method. Moreover, since it is a thin film firmly bonded to the sublayer/substrate, the monolayer can eliminate pattern collapse due to the capillary force when using liquid development, which is a serious concern for spin-coated (thick) resists. Another advantage for a polymer monolayer coating method over spin-coating is the lack of edge-bead effect, which is also a serious problem for spin-coating.[27] It is thus suitable for patterning on ultrasmall substrate without having any edge-bead effect.

2. Results and Discussion

We first examined whether the PMMA that contains 1.6% methacrylic acid (MAA) monomer still behaves as positive e-beam resist. We exposed a 7 by 7 square array at 3 keV with exponentially increasing doses from 9 to 900 μC cm⁻². As shown in Figure 1a for three consecutive squares, the squares exposed in a spin-coated thick film were dissolved by 30 s MIBK (Methyl Isobutyl Ketone) : 2-proponol (IPA) development, thus confirming that the MAA addition did not alter significantly the positive resist property. As a matter of fact, P(MMA-co-MAA) with MAA content up to 40% has been demonstrated as positive resist with sensitivity higher than that of pure PMMA,[29] and this sensitivity difference makes the bilayer structure PMMA/ P(MMA-co-MAA) widely utilized to create an overhang profile in order to greatly facilitate the subsequent liftoff process.[30] Furthermore, the methacrylic acid can also be replaced with its metal salts to give a metal-containing PMMA-based resist having very high dry etching resistance.[31]

We then characterized the monolayer PMMA and the developed square patterns are shown in Figure 1b–d. As expected, MIBK:IPA can be used as developer for the monolayer resist (Figure 1b). But unlike thick PMMA film for which acetic acid is a good solvent thus cannot be utilized as a developer, here acetic acid is an effective developer for the monolayer resist (Figure 1c), which is not surprising because the unexposed PMMA monolayer can no longer be dissolved by acetic acid when firmly anchored to the substrate. Interestingly, when the exposure dose is very high, the exposed PMMA brush can hardly be dissolved by acetic acid (Figure 1d). This is consistent with the well-known fact that PMMA becomes negative resist (cross-linked thus insoluble) at very high exposure dose,[32] which is because that, upon exposure, both chain scission and chain cross-linking occurs in PMMA, and the latter dominates at very high doses. Here the developed thus recessed “frame” surrounding each square is formed due to moderate exposure in the positive tone regime by proximity effect. Despite the very low thickness of the monolayer resist, we managed to obtain an approximate contrast curve by AFM measurement as shown in Figure 2. The contrast curve again indicates that the monolayer PMMA first behaved as positive resist, and then turned into negative tone at dose beyond roughly 200 μC cm⁻². In addition, unlike thick PMMA film, there was a sharp drop of remaining thickness at the initial low doses, presumably because the chain segments become soluble once cut off from the substrate, even though PMMA (when existed as a thick film with the chains entangled) with the same molecular weight as the chain segments would be insoluble in the developer.

Next, the P(MMA-co-MAA) with a molecular weight (\(M_n\)) of 15 kg mol⁻¹ contains 1.6% MAA, or on average 2.4 MAA units per copolymer molecule. The packing density \(\sigma = (hN_d)/M_n\)
(Nv is Avogadro number) can be calculated for a monolayer thickness of h = 9 nm and density, ρ = 1.18 g cm−3 as 0.426 chains per square nanometer. This chain density lies in the high density packing regime (more so when noting that each chain contains 2.4 grafting sites) for PMMA that has a theoretical maximum density of ρmax = 1.5 nm−2.[33] To achieve even higher packing density, “grafting from” approach,[34] for which the polymerization is carried out in situ on the substrate surface, may be utilized. However, “grafting to” approach is preferred here since it works well enough for our application; and more importantly, it is much more convenient than the “grafting from” approach since spin- or dip-coating and subsequent thermal annealing is far simpler than chemical synthesis to form the polymer brush each time on a substrate. Last, though P(MMA-co-MAA) that contains –COOH group might conceivably form a chemical bonding to –OH terminated substrate with the release of water, just in the same way as the –OH terminated PMMA-poly styrene to –OH terminated substrate popularly employed as a neutral surface layer for block copolymer self-assembly,[25,26] we were not able to confirm the formation of chemical bonding. Some previous reports seem to suggest that carboxyl group may not bond chemically to hydroxyl terminated substrate directly; and in order to form a strong, permanent chemical bond, the authors first modified the substrate with an epoxysilane self-assembled monolayer[35] or poly(glycidyl methacrylate) that contains epoxy groups pendent to the main chain[36] or functionalized the carboxyl end group so as to convert the carboxyl terminated polymer into triethoxy silane terminated polymer since the silane will react readily with the –OH terminated substrate.[37,38] However, another report demonstrated the formation of chemical bonding between carboxyl group in the polymer and hydroxyl group on the substrate with the grafting reaction having an enthalpy of +7.4 kcal mol−1.[39] Regardless of the grafting mechanism, it was found that our grafted PMMA monolayer adhered strongly to the substrate and could not be dissolved by hours of soaking in a solvent, enough to serve our purpose as a stable monolayer resist.

To study the resolution capability of the PMMA monolayer, we exposed periodic dense line arrays with periods from 300 nm down to 100 nm. The lines were written by e-beam exposure at a voltage of 3 kV with a step size of 5 nm. After pattern transfer into Al film then into silicon. Figure 3 shows the SEM images of grating patterns with a line dose of 31 pC cm−1 and periods of 200 nm (a) and 100 nm (b) fabricated on the flat part of the AFM cantilever (silicon). Grating patterns with periods of 200 and 100 nm are clearly well-defined with good contrast. The line-width resolution (here isolated line) is down to 30 nm, as shown in inset of Figure 3b. Resolution is higher for thin monolayer film than much thicker spin-coated film because there is less proximity effect and less pattern collapse due to capillary force.

Figure 4 shows the SEM images of dense grating arrays fabricated on nonflat region of AFM cantilever with period of 200 nm, which clearly demonstrated the capability of our method for nanofabrication on irregular surfaces. Besides resist coating, there are also several other issues to consider for nanofabrication on nonplanar samples. First, dose on side-wall is reduced by a factor of cosθ, where θ = 60° is the slope angle; and the grating period is enlarged by a factor of 1/cosθ. Second, for patterning on the sloped surface, the electron beam may not be well focused across the entire exposed surface area, which will lead to beam enlargement and distortion. Therefore, the resolution of nanostructures on the cantilever side surface depends on the depth of focus of the electron beam in...
EBL system. Ignoring the wave nature and diffraction of the beam, the depth of focus is inversely proportional to the aperture size and proportional to the working distance (WD) in EBL system. Thus, like typical camera, higher depth of focus is achievable using a smaller aperture size or a longer WD. However, one drawback for using smaller aperture is longer exposure time because of lower beam current that is roughly proportional to the square of the aperture size of the SEM system. As an example to give an idea of effect of depth of focus, in our previous work we achieved 80 nm resolution (suggests beam spot size ≈60–70 nm) when the beam was out of focus by 37 µm with 30 µm aperture size. Here the cantilever thickness is ≈10 µm, thus the electron beam should be reasonably well focused on the entire cantilever sidewall.

Third, our process involves Al film deposition by evaporation; and in vacuum deposition system, the metal film thickness is proportional to cosθ, thus the film is thinner on the cantilever side surface. In order to obtain better uniformity of metal film on the top and side surfaces of the tip, the tip could be mounted on a rotating support. Fourth, our process involves Al and Si etching; and the dry etching rate and direction may depend on the surface slope angle relative to the electrode of (RIE) system, the self-formed bias voltage tends to be normal to the “local” surface, thus the etching is largely perpendicular to the local surface even though the surface is not parallel to the electrode.

3. Conclusions

We demonstrated the feasibility of using PMMA monolayer “brush” as an e-beam resist to carry out nanofabrication on irregular surfaces. By spin- or dip-coating followed by thermal annealing and solvent removal of bulk (nongrafted) polymer, we successfully grafted PMMA (contains methacrylic acid) on modified nonflat surface with a monolayer thickness about 9 nm. As a proof-of-concept of patterning on nonflat surface, we fabricated grating structures on the AFM cantilever using this brush monolayer as resist and Al as hard mask intermediate layer. High resolution down to 30 nm line width was etched into AFM cantilever. Nano-patterning on nonflat substrates may find applications in fields such as AFM TERS for chemical analysis and lab-on-fiber technology.

4. Experimental Section

To form a grafted monolayer resist, a low-molecular-weight PMMA was chosen that contains 1.6% MAA to promote the grafting process as MAA contains the desirable –COOH group (Sigma-Aldrich, poly(methyl methacrylate-co-methacrylic acid), Mn 34 kg mol⁻¹ and Mw 15 kg mol⁻¹). As an example of nonflat surface, silicon AFM probes (Nanoworld Arrow probe) were chosen to demonstrate the capability of patterning on nonflat surfaces by grafting the monolayer resist, noting that AFM tip is typically used in TERS.

Figure 5 shows the schematic fabrication process steps. The sample surface was first cleaned by IPA, followed by oxygen plasma cleaning for 1 min (20 sccm O₂, 20 mTorr pressure and 20 W RF power). For easier handling, the AFM tip was attached to a piece of regular silicon wafer by using photoresist as a “glue”. To transfer the pattern into the substrate by dry etching, a hard etch mask of thin (5–9 nm) aluminum (Al) film was deposited onto the AFM probe with a chamber background vacuum of 2 µTorr using an Intlvac vacuum deposition system. During metal deposition, the heating power was increased slowly until a desired deposition rate of ≈0.5 Å s⁻¹ was achieved. To form a monolayer, PMMA dissolved in anisole with a concentration of 1 v/v% was coated by dip (for nonplanar surface) or spin (planar surface) coating on the samples that were cleaned by solvent and treated with oxygen plasma. Next, the resist was baked for 24 h at 160 °C on a hotplate to induce the grafting between the resist and hydroxyl terminated silicon substrate (or substrate coated with an aluminum thin film). Finally, the bulk of PMMA was washed away by rinsing with acetic acid, leaving behind a monolayer “residual” brush.

Electron beam lithography was conducted using a Leo 1530 FE-SEM (Field-Emission Scanning Electron Microscopy) system with 3 kV acceleration voltage and 10 pA beam current (30 µm aperture). The exposed resist was developed by MIBK:IPA (1:3) for 7 s, except for the overexposed case where longer development times were needed to show any measurable dissolution. Such a very short development time is enough to develop the monolayer resist. After development, the pattern was first transferred into the aluminum film using PAN etching (PAN etch recipe: phosphoric acid:nitric acid:acetic acid:DI (De-ionized) water = 16:1:1:2) at room temperature for 5 s, followed by washing with DI water. Next, the pattern in Al film is transferred into bulk silicon by dry etching (ICP RIE, Trion PI system with the recipe of 40 sccm CF₄, 3 sccm O₂, 8 mTorr pressure, and 50 W RF power) for 30 s. Finally, the pattern was observed by using either LEO 1530 FE-SEM or Zeiss Ultra FE-SEM.