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Tilted nanostructure fabrication by electron beam lithography

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Periodic tilted nanostructures over large area have various applications. In this work tilted nanostructures were created by SEM scanning of electron beam resists with the substrate tilted at 45°. The key to the process is the usage of the dynamic focus function that is available for most SEM systems for imaging purpose (but not for lithography), as otherwise the tilted substrate will be out of focus of the electron beam. The pattern created by this method is limited to periodic pillar or hole array using negative or positive resist, respectively, with the number of pillars or holes per scan given by the image resolution (e.g., 1024×768). The diameter of the pillars or holes was determined by the exposure dose, which is in turn determined by the beam current and scan speed (scanning time per frame). The array period is controlled by the magnification (that determines image area, e.g., 1 mm^2) and image resolution. The pillar or hole pattern in the resist can be further transferred to another material such as Au by electroplating. © *2012 American Vacuum Society*. [http://dx.doi.org/10.1116/1.4754809]

I. INTRODUCTION

Tilted micro- and nanostructures have various applications due to their directional and anisotropic nature of the surfaces. For example, tilted periodic pillars in soft materials like polydimethylsiloxane (PDMS) is important for the study of directional cell movement,[1] and surface enhanced Raman spectroscopy,[2] as well as artificial surface mimicking gecko feet with unidirectional frictional force for dry adhesive pads application.[3–5] Tilted nanostructures can also be employed for directional adhesion and wetting[6,7] or introduced into photovoltaic device to avoid a short circuit between the two electrodes.[8]

Microscale tilted structures can be fabricated readily by using contact or proximity photolithography with the substrate tilted because the depth of focus for collimated UV light is effectively infinite.[3,9,10] Though projection photolithography using deep UV light can achieve sub-100 nm resolution, it is not suitable for tilted substrate due to the very low depth of focus. Previously nanoscale tilted structures have been fabricated by reactive ion etching with tilted substrate; however, modification of the etching system, notably the addition of a Faraday cage, is needed, as otherwise the spontaneously generated self-bias field in the plasma (that determines the etching direction) would remain normal to the substrate surface.[11] Tilted silicon structures can be created by anisotropic metal assisted chemical etching,[8] yet this process is not stable and zigzagged silicon pillars may form since there are several equivalent crystalline directions.[12] Glancing angle deposition (GLAD) can be used to form tilted pillars that is an amplification of the otherwise grain structure, though it lacks control of the pillar spacing or diameter.[13] Tilted polymer nanostructure can also be created with a molding process by changing the angle of release from the template.[14] Alternatively, straight polymer pillars can be deformed to form tilted ones by processing the patterned film through two heated rollers.[15] In addition, electron or ion beam irradiation from the side can be used to bend polymer or even metal pillars due to stress or uneven shrinkage of the irradiated surface and the opposite surface, resulting in tilted pillars.[4,16,17] Evaporation of a metal layer onto one side of polymer pillars followed by thermal annealing can bend the polymer pillars due to stress resulted from mismatch in thermal expansion coefficients between metal and polymer.[18]

In principle, one can fabricate tilted nanostructure by electron beam lithography with tilted substrate using laser auto-focus; however, in practice this could be very time consuming. This is because the depth of focus of the electron beam is typically on the order of 10 μm, and thus each write field has to be in the same order for 45° tilt angle in order to maintain focus within each write field, which leads to tens of thousands of write fields over an exposure area of 1 mm^2 and thus very long stage movement and focus adjustment time. In this work, we report that 2D periodic array of tilted nanostructure can be conveniently fabricated through SEM exposure of an electron beam resist during normal imaging of a tilted resist-coated substrate using the dynamic focus function, which is designed to maintain the focus across a tilted substrate by adjusting the working distance continuously during scanning. Since the exposure is carried out in the imaging mode, there is no need of pattern generator or beam blanker. The main limit of the current approach is that only 2D periodic structures can be fabricated.

II. EXPERIMENT

ZEP-520A was chosen as positive resist that leads to 2D hole array pattern after exposure and development. The resist (as purchased or diluted by anisole for thinner film) was spin-coated on a silicon wafer and baked at 180 °C for 10 min. For negative resist that leads to pillar array pattern, chemically amplified resist SU-8 diluted by cyclopentanone was spin-coated to achieve a film of ~500 nm and pre-baked at 90 °C

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on a hotplate to drive away the solvent; chain cross-linking resist polystyrene with molecular weight of 260 kg/mol is dissolved in chlorobenzene at 10% concentration to achieve ~800 nm-thick film after spin coating.[19,20] A LEO 1530 FE-SEM was used to expose the resist at 20 kV acceleration voltage and 0.1 ~ 2.5 nA beam current. Pixel average was chosen for noise reduction that is advantageous over line average or frame average because the electron beam was found not to go to the exact pixel location when the scan area is on the order of 1 mm. For the same reason, each exposure was carried out using only one scan. The scan speed was set such that the scanning time per frame was 0.1–1.0 min depending on beam current and resist sensitivity. The substrate was typically mounted on a 45° stub. In the experiment, the image center was first focused at high magnification by adjusting working distance as usual. Then magnification was reduced to match the target scanning area, and a small viewing window is opened at the top (or bottom) of the image. Next, with the working distance fixed, the amount of tilt compensation is adjusted until the clearest image was obtained at the top (or bottom) of the frame. Finally, the resist was exposed by one full-field scan. The number of holes or pillars thus fabricated is the same as the image resolution. The array period along the horizontal direction is equal to scan field size (inversely proportional to magnification) divided by the number of pixels along the horizontal direction and that along the vertical direction also depends on the tilt angle. For instance, with a scan field size of 1000 μm along the horizontal direction ($1000/1024 \times 768 = 750$ μm along the vertical direction), image resolution of 1024×768, and substrate tilt angle of 45°, the array period along the horizontal direction is $1000/1024 = 0.977$ μm and that along the vertical direction is $(750/768)/\cos(45) = 1.381$ μm.

Exposed ZEP-520 A films were developed by n-amyl acetate for 1 min, exposed SU-8 films were postexposure baked at 90 °C on a hotplate for 1 min before development using propylene glycol monomethyl ether acetate (PGMEA) for 2 min, and exposed polystyrene was developed using xylene for 2.5 min. One way to transfer the pattern in the resist to another layer or material is electrodeposition of a metal into the resist template. The wafer was coated with Cr/Au as conduction layer before spin-coating ZEP-520 A resist. After exposure and development, the sample was treated with NaOH solution for 1 min to remove possible grease, followed by HCl solution for 3 min to depassivate the surface. Au electroplating was carried out using a commercial cyanide-free bath at 60 °C with 2.0 V constant voltage for ~3 min. After electroplating, the sample was rinsed with DI water, followed by soaking in anisole to remove the ZEP-520 A resist. Another way of pattern transfer is cast-molding of PDMS onto the resist template, and this process is currently under study.

III. RESULTS AND DISCUSSION

Figure 1 shows the cross-sectional view of the tilted holes in 100 nm ZEP resist (ZEP-520 A diluted with anisole at 1:1

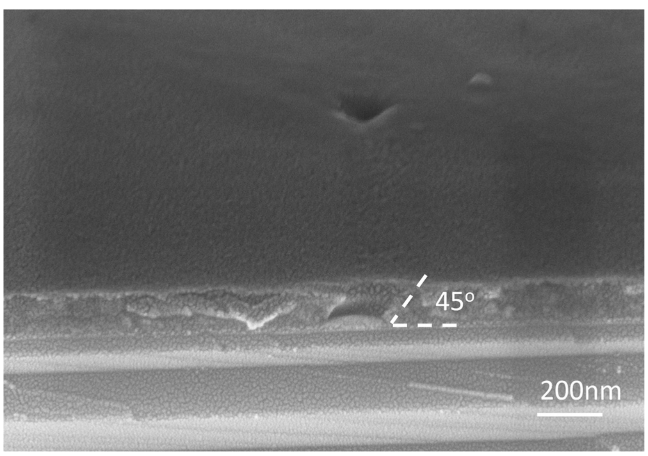

FIG. 1. SEM images of 45° tilted hole array in 100 nm-thick ZEP-520A resist.

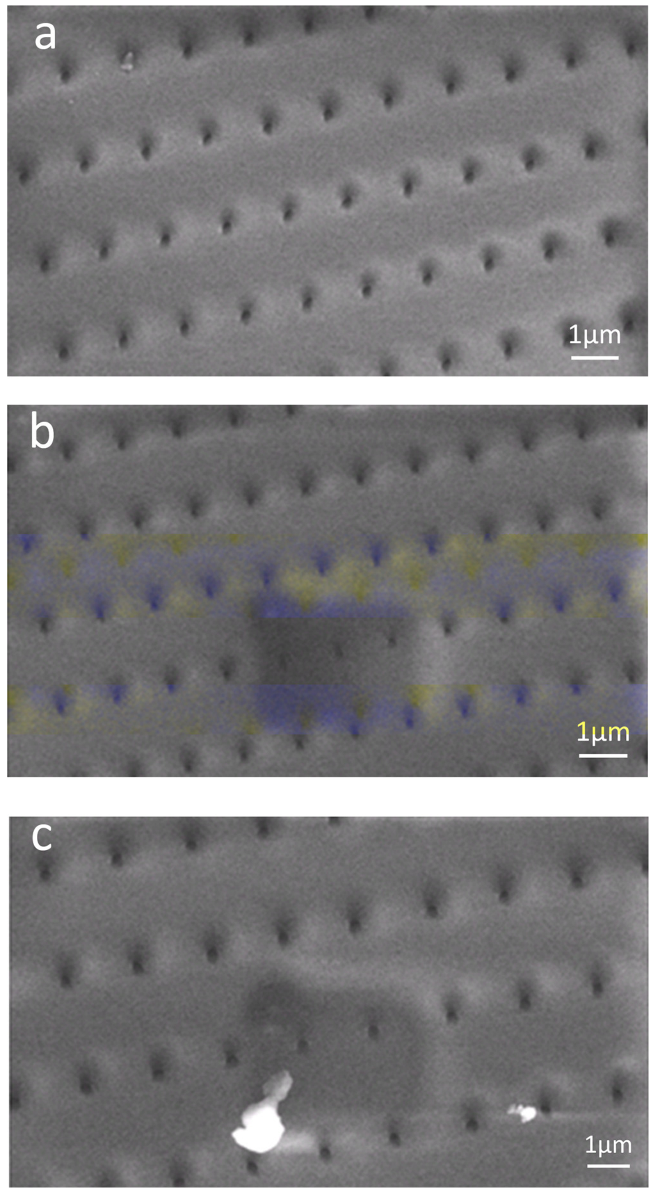

FIG. 2. (Color online) Top view SEM images of 45° tilted hole array in 645 nm-thick ZEP-520A showing hole-size uniformity across the pattern area of ~1 mm. The images were taken on the bottom-left corner (a), center (b), and top-right corner (c) of the scanning area.

ratio) exposed with the sample tilted by 45° at the beam current of 100 pA. The exposure dose per dot is calculated to be around 10 fC/dot. As expected, the hole diameter is rather uniform across the entire pattern area of ∼1 mm when using the dynamic focus function (see Fig. 2). Though ZEP-520 A is a high resolution resist with sub-20 nm resolution readily achievable when using normal electron beam lithography (EBL), here the resolution is limited to roughly 100 nm by the beam positioning accuracy and stability when using large scanning field of ∼1 mm that is one order larger than that for typical high resolution EBL. It is possible to generate holes larger than 500 nm by using significantly higher dose. In fact, the hole size is ultimately determined by the point spread function of the electron trajectory that predicts an exponential relationship between point dose and hole size. For instance, holes of diameter 600–700 nm (not shown) were formed when using a very high beam current of 2.3 nA.

Tilted nanopillar array was resulted using negative resist SU-8 [Fig. 3(a)] that is about 20× more sensitive than ZEP-520 A and polystyrene [Fig. 3(b)], whose sensitivity can be tuned easily by using different molecular weights (about 2× more sensitive than ZEP-520 A for 260 kg/mol).[20] The pillar is larger at the bottom than the top, which is due to strong forward scattering of the incident electron beam and (for SU-8) the very low contrast (contrast $\gamma \sim 1$). In fact, forward scattering of the electron beam is more serious for tilted incidence than for normal one [partly because of the increased trajectory by 1/cos(tilt angle)].

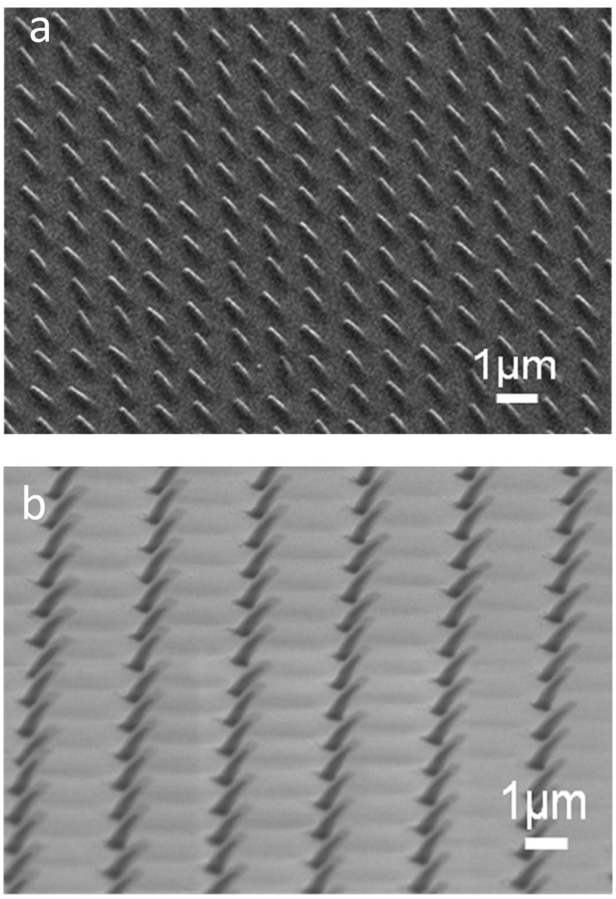

FIG. 3. SEM images of 45°-tilted pillar array in 500 nm-thick SU-8 resist and 1000 nm-thick 260 kg/mol polystyrene resist. The pillar base is larger than the pillar top due to strong electron forward scattering. The array period is about 1 μm for SU-8 and 2 μm for polystyrene.

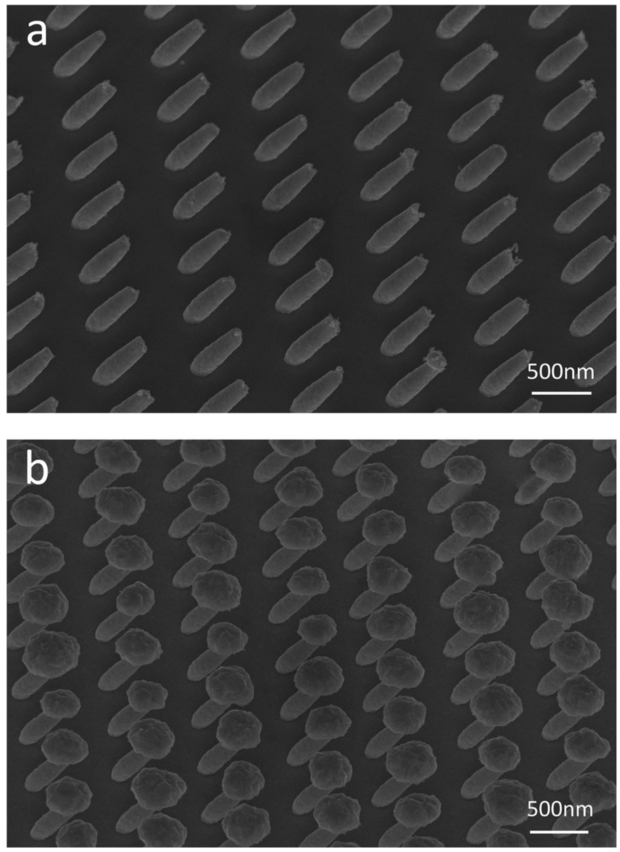

FIG. 4. SEM images of 45° tilted Au pillar arrays by electroplating into tilted hole arrays in ZEP-520A resist. (a) Tilted pillars of ∼300 nm diameter and ∼750 nm length without Au over-plating. (b) Mushroom shaped Au pillar array due to over-plating. The images were taken at 45° viewing angle.

To fabricate tiled nanopillars, as well as to reveal the profile of the holes, we carried out Au electroplating into the hole array in ZEP and subsequently removed the ZEP resist using anisole. The 45° tilted Au pillar array with length of ∼750 nm sitting on top of Cr/Au plating base layer is shown in Fig. 4. Tilted mushroom-shaped pillars with a "cap" were resulted when the holes were over-filled with Au.

IV. CONCLUSIONS

In this work, we demonstrated that 2D periodic array of tilted nanostructure can be conveniently fabricated by SEM exposure of an electron beam resist using normal imaging mode, without the need of pattern generator or beam blanker. Actually, the regular EBL system will not work for this purpose because the focus cannot be maintained within the entire write field when the substrate is tilted at large angle, unless very small write field of ∼10 μm is used that would lead to very long exposure time to pattern an area of order 1 mm^2. We made use of the dynamic focus function that is available to typical SEM systems, whereby the working distance is adjusted continuously during the scanning of a tilted sample in order to maintain focus across the entire imaging field that can be several millimeters depending on the magnification. The number of tilted structures thus fabricated within one viewing field depends on the image resolution (such as 1024×768), and the array period is determined by the image resolution and magnification (and tilt angle for the period along y-direction). Exposure dose is determined by the beam current, scan speed, and the number of pixels. Hole and pillar arrays of 100 s nm diameter and $\sim 1\ \mu m$ periodicity were achieved for positive ZEP and negative SU-8 and polystyrene resist, respectively. Au pillar arrays of similar size were fabricated by electro-deposition into the hole array.

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