Fabrication of ordered nanospheres using a combination of nanoimprint lithography and controlled dewetting

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Arrays with hemispherical dots were produced from nanoimprinted line structures by thermal reflow and coagulation. By adding local nodes into 100 nm wide line cavities of the nanoimprint stamp, the coagulation was controlled and a self-ordered, highly regular dot matrix with almost totally dewetted lines was obtained. The forming of dots of almost equal sizes and distances along the line's location shows that this coagulation effect is probably only restricted by geometry and surface energy. Simple resist preforms can be transformed into a more complex pattern by thermal-postprocessing in a controlled way. © 2010 American Vacuum Society.

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I. INTRODUCTION

Reflow of resist structures by melting is a powerful post-processing method for the generation of three-dimensional (3D) structures with defined spherical and cylindrical shapes.¹ It uses resist melting and mass-transport to modify the shape of a binary resist structure fabricated by photolithography into a 3D shape. When heated over its glass transition temperature T_g , the photoresist changes into a viscous state and surface tension leads to formation of a surface of least energy (surface of minimum area). It has also been used for the fabrication of nanoscale gratings with reduced line edge roughness, gap narrowing, and aspect ratio enhancement.² Thus it becomes an attractive postprocessing method which enhances the scope and flexibility of current nanofabrication.

In this contribution, we enlarge the portfolio of reflow even further by forming new structures by controlled dewetting and agglomeration. In contrast to binary photolithography, we use nanoimprint lithography (NIL) for the formation of polymer nanostructures prior to reflow. This is because of its range of shapes and materials along with high resolution capability.³ The main difference to photolithography is the fact that it needs an additional etching step to remove the residual layer and to open windows on the substrate. The plasma treatment changes the surface properties of the substrate surface significantly. After window opening, it becomes hydrophilic which enhances the ability of the resist to wet and spread into areas previously not covered. This spreading is reduced by an additional hydrophobic surfactant coating before annealing the sample.⁴ Surprisingly, hydrophilic and hydrophobic coatings seem to work in an analogous way for polymers such as poly (methyl methacrylate) (PMMA), i.e., a low contact angle for a plasma activated

surface, and a high contact angle is achieved for a surfactant coated surface. However, for ridges with a line width of 100 nm, we then observe a dewetting of resist during reflow.⁵ The resist, which normally tends to spread laterally to some extent over the areas covered by the surfactant, splits locally and collects material along the ridges to form larger hemispherical dots. Since the material is not able to flow large distances, local depletion happens and dots are formed along the lines which are almost randomly distributed [see schematic in Fig. 1 and atomic force microscopy (AFM) micrograph in Fig. 2].

We have now found a way to control this spontaneous coagulation of material, by adding nucleation points into the original pattern. In this contribution, we analyze the forming of the dots from linear ridges and show how stamps for NIL can be fabricated in an easy way with regular arrays of 3D structures with hemispherical shape.

II. EXPERIMENT

The NIL molds have been fabricated with electron beam lithography (EBL) exposure in a Vistec EPBG 5000+HR at 100 keV, using standard process routes in a classical PMMA EBL resist (Allresist AR-P 679.04) with a molecular weight M_w of 950 000 g/mol and reactive ion etching (RIE) of the silicon substrate. In the case of molds with defined nucleation points, for a line width of 100 nm, circular bumps with a diameter of 120 nm were placed as nodes along the lines (see Fig. 3). The stamps were coated with an antisticking layer, based on molecular vapor deposition (MVD) using fluorinated silane chemistry.⁶

All preform structures have been fabricated by thermal NIL, in the classical PMMA NIL resist with a molecular weight of 25 000 (glass transition of PMMA T_g 105 °C, imprint at T_{imprint} 180 °C). This process is well described in some of our previous publication.⁵ After imprint and demold-

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FIG. 1. (Color online) Process scheme: Polymer line structures are generated by nanoimprint lithography and window opening before a hydrophobic surfactant coating is applied. Depending on minor modification of the stamp design, (a) randomly distributed dots or (b) a regular pattern is formed during a subsequent reflow step.

ing, the structures were thinned down and substrate windows were opened by anisotropic RIE using oxygen plasma. As a hydrophobic coating, we applied our standard MVD process at room temperature directly after the RIE process.⁶ Since this process generates a very thin (<2 nm) homogeneous coating without large quantities of nonbound excess silane, we proceeded without removing the residual silane on the substrate or resist. The thermal reflow was performed on a hot plate in ambient conditions at a constant temperature. Then the resist was hardened by instant cooling, when the desired shape was achieved. Since we were interested in time-dependent evolution of the reflow, the investigations were carried out at moderate temperatures of 160°C to avoid rapid collapsing of structures and to observe structure evolution over time. AFM was used for shape analysis. For reflow, however, long reflow times were needed, since the coagulation effect was starting after a few minutes but took up to 16 h until a final equilibrium was found.

III. RESULTS

An interesting correlation for the formation of dots was found in the first experiments with surfactant coated ridges,⁵ which was based on the assumption, that coagulation is directly linked to the tendency of a polymer ridge to spread on a hydrophobic substrate. For a substrate with hydrophobic properties, this would happen if the aspect ratio exceeds the

FIG. 2. (Color online) AFM micrograph of dewetted polymer ridges (100 nm width and height) on a silicon substrate with hydrophobic coating after 16 h of reflow at 160°C , resulting in semiordered hemispherical polymer dots along the lines.

FIG. 3. SEM micrograph of a silicon stamp showing nodes along 100 nm wide line cavity (detail in insert). The period of nucleation points is 500 nm.

factor of 0.25. At a preform height of 100 nm, as used in this work, this is actually the case for ridge widths below 400 nm and therefore certainly applies for the 100 nm wide ridges investigated here. It was also deduced that coagulation was induced by singularities, i.e., borders, defects, and roughness, which would be similar to the formation of capillary bridges during NIL.⁷ This can be seen in Fig. 2, for a line grating with a period of 250 nm, where line ends can be identified as seed points of a first row of hemispheres (here called dots or balls). However, a closer look shows that the dots are not forming at the end of the original ridges, but at a defined distance (around 200 nm) measured from the line ends. Furthermore, the size (240 nm) and height (56 nm) are quite similar for these dots. This can be attributed to the simple fact that due to volume conservation, the same amount of material was accumulating at each line. Obviously, this is drawn away from the line areas connected to the dots which were now almost depleted. Interestingly, the lines are not completely erased (with a residual layer of 10 nm thickness), from which we learn that the process of dot formation (coagulation) is self-limiting. The second row of dots in Fig. 2 is located at distances between 200 and 500 nm from the first row. It can also be seen that the size of the dots is dependent on their distance from the next neighbor along the line. As with the first row, volume conservation therefore seems to be the reason for the size of the dots, but in contrast to this, their locations and consequently sizes are only defined within some range. All dots seem to be slightly oval, stretched along the line, which can be attributed to the better wetting in the direction of the lines still covered by a residual polymer layer.

This semichaotic ordering was the basis for the inclusion of defined seed points along the imprinted lines. Due to the writing capabilities of or EBL system, nodes could be easily inserted into the line cavities within the Si mold, with only a minor increase of writing time. If these nodes were set in distances smaller than the average distance of dots forming without nodes, we obtained a regular dot matrix (Figs. 4 and

FIG. 4. (Color online) AFM micrograph illustrating an orthogonal matrix of regularly sized dots (the dot period is 500 nm, and pitch of the original lines is 500 nm).

5) with almost totally dewetted lines. A node distance of 500 nm was chosen for reflowing 100 nm wide and 100 nm high ridge preforms. This results in an array of regularly ordered structures with identical shapes and sizes (see Fig. 5). The height of the structures is 65 nm. This regular ordering was also confirmed for node distances of 1000 nm. The interesting fact is that due to the choice of distance, the height of the final lenslike structure can be controlled.

The lenslike resist structures were used as template for stamp fabrication. Figure 6 shows the transfer of the 3D resist structures into silicon using a standard RIE process developed for proportional pattern transfer. The inductively coupled plasma RIE (Oxford ICP 100) etching process had an etch rate of 50 nm/min. The etched silicon patterns can now be used as stamp originals or for the fabrication of stamp copies, e.g., by generating OrmoStamp[®] replications.⁸

FIG. 5. SEM micrograph showing matrix of 250 nm wide hemispherical dots with a pitch of 500 nm (the pitch of the original lines is 500 nm).

FIG. 6. SEM micrograph of silicon substrate with hemispherical dots after pattern transfer using anisotropic RIE (the pitch is 500 nm in both orthogonal directions).

IV. DISCUSSION

The main advantage of the combination of NIL and reflow lies in the fact that 3D structures with defined shape can be generated from two-dimensional resist structures in a controlled way on large areas. Apart from obvious advantages as the reduction of surface roughness, postprocessing by reflow can also be used to generate new kinds of patterns. A possible application is the fabrication of arrays of nanospheres with defined shape and low edge roughness for magnetic nanodots with perpendicular anisotropy.⁹

Is there any advantage in comparison to the use of direct patterning of nanodots by EBL and NIL? At this time, there are only preliminary answers to this question. First, dotlike structures with high aspect ratio are more difficult to imprint than line structures. The polymer does not easily fill the tube-like cavities of structures, and also the demolding becomes more difficult due to the high surface to volume ratio.¹⁰ In the case of reflowed cylinder structures in resist, i.e., lenslike structures with low rim inclination, this would be much easier. Therefore, the main advantage of the concept lies in the fact, that due to accumulation and depletion, EBL writing times of specific structures needed for reflow, such as dot arrays in positive resist, can be reduced. Negative structures such as holes are much easier to expose, but more difficult to imprint.¹¹ An interesting point is that in the future, for large area structuring, it is better to start with stamps with regular line grating structures, e.g., made from interference lithography, and build-up desired geometries from them. Then we can think about starting with a grating structure with defined line size and pitch, and adding locally some auxiliary nodes. Here, the aim is that only few nodes have to be set which work as nucleation points. Future research will determine the size and distances for different line widths and node locations, and clarify the role of the nodes for nucleation.

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