Complementary Analysis of Metallic Templates Fabricated by Nanosphere Lithography

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We present a comparative microscopic study on metallic templates prepared by nanosphere lithography. Scanning electron microscopy, low kV Energy dispersive X-ray spectroscopy, scanning ion microscopy, atomic force microscopy and confocal Raman spectroscopy were used to analyse the assembly of the nano-templates. Contact angle measurements allowed us to optimise the surface treatment of the Si substrate to obtain maximal spreading and regularity of the nanosphere arrays. After metal deposition and toluene nanosphere removal, we found the expected interstitial triangular structures, originating from the 2D single layer hexagonal sphere array. We also detected a number of other features such as rings, circles, cups and lines which were found to be generally positioned below the nanospheres. A review of proposed mechanisms and the various analysis performed here indicate that some of these features are partly polymeric and partly caused by residual material leaching out of the nanospheres at various stages of the process. [DOI: 10.1380/ejssnt.2009.341]

Keywords: Nano-rings; Nanosphere lithography; Atomic force microscopy

I. INTRODUCTION

Well-defined nanoscale templates are promising candidate for fast and cheap assembly of nanodevices like high-density data storage [1, 2], biological biosensors [3–5], medical diagnosis [6] and microelectronics [7]. Over the last few decades, efforts have been made to improve the homogeneity and growth of these templates using a variety of preparation methods. The one of interest in this study is Nanosphere Lithography (NSL) [8–10]. It is based on the self-assembly of nanospheres onto a substrate, subsequent metal deposition and nanosphere dissolution, using an appropriate solvent. The main nanostructures found for a single-layer arrangement are triangular features organized in a 2D array, although other features such as dots, rings, cups, etc are also found [11]. Nonetheless, a number of challenges remain. Firstly the growth of defect-free assembly over large area is still problematic, especially for surfactant-free methods which are often preferred as they leave fewer residues. Secondly, there are many microscopic investigations but very few detailed analytical studies of these materials, often these studies assume that any features observed by the microscope are deposited metal. What is presented here is a comparative study using a number of microscopic and analytical techniques to challenge this assumption and understand better the mechanisms of NSL template formation.

The simplest NSL protocol is to cast a few 10 microliters of the colloidal solution onto the substrate and to leave it to dry. This usually leaves a ring-like area of multilayer assembly (coffee-drop effect), around which monolayer regions can be found. A variant of the drop-casting technique is to use a small motor and a flexible Teflon membrane to define a slow moving contact line which gives more regular assemblies [12]. Another method is spin-coating, where the speed (rpm) must be adjusted to the particle size and to the concentration. Some studies have also focused on modifying the surface of the nanosphere using plasma treatments [13–15] or on using surfactants to obtain larger defect-free arrays [16].

In this paper, we mainly focus on the analysis of the nano templates and, therefore, we settled for a simple drop casting preparation technique onto a silicon substrate which gave consistent results. The metal nanostructures were prepared using magnetron sputtering. These nanospheres were consequently rinsed with Toluene solution. The analysis were made at various stages of the process by Scanning electron microscopy (SEM), low kV Energy dispersive X-ray spectroscopy (EDX), scanning ion microscopy (SIM), atomic force microscopy (AFM) and confocal Raman spectroscopy. The surface treatment of the Silicon substrate was optimised using contact angle analysis to achieve monolayer assembly over large areas. The expected single features typically encountered in nanosphere lithography were observed. In addition, other features (rings, circles, cups, etc.) were also detected and are discussed using the various analytical techniques mentioned above.
II. EXPERIMENTAL

A. Sample Preparation

Polystyrene (PS) nanospheres of diameter 499 ± 5 nm were purchased from Duke Scientific Corporation. Approximate concentration in water is 1g PS in 100 ml of distilled water (~1wt%). These nanospheres are expected to be made of high molecular weight (~2 × 10^6 g/mol; i.e. 19203 monomer units) although their polydispersivity is unknown. Silicon substrates (100) were cut into small pieces 1 × 1 cm². The average surface roughness for 5 μm AFM scans was Rₙ ≈ 0.4 nm. Each square was treated with piranha solution (concentrated H₂SO₄ solution (70%) mixed with H₂O₂ in a 3:1 ratio) to remove contamination from the silicon substrate and double-rinsed with distilled water in an ultrasonic bath for 30 minutes. This surface treatment resulted in a slight smoothing (Rₙ ≈ 0.2 nm). A small volume (20 μl) of nanospheres was dispensed on tilted (~4°) Si substrates [17] to optimize monolayer coverage. RF Magnetron sputtering system was used for the deposition of 60 nm cobalt film. The base pressure was 1 × 10⁻⁷ mbar, growing to 10⁻³ mbar during deposition with the plasma power set at 90 W. We also used temperature sensitive labels (RS components), positioned on the substrate plate to monitor the highest reached temperature during deposition, as a physical deposition process such as magnetron sputtering could result in a slight heating of the samples. Evaporation rate was 1 Angstrom per second, estimated using an oscillating quartz crystal and precisely measured by post-deposition AFM measurements. The system geometry is as follow; a 3 cm diameter Cobalt target situated 17 cm from the substrate plate to monitor the high set point (gentle tapping regime) with 512 pixels and 1 Hz scan rate. Since most of the expected NSL features are submicron in size, and as for any extensive AFM study, tip wear cannot be completely ignored, we used a blind reconstruction algorithm (SPIP software from Image metrology S/A.) to extract the possible effect of tip convolution. Mostly, we found little difference between the raw and de-convoluted images. We also used specific AFM techniques to track differences in surface properties such as stiffness and adhesion, firstly using the lift-mode/interleave option of the Veeco software, secondly using digital pulse force mode (DPFM) from Witec Gmbh. In the Veeco interleave lift mode one AFM line is scanned in the normal manner, the next line is scanned with the feedback off, at a preset height above the surface and using the topographic information from the previous line to “follow” the surface, displaying either phase or amplitude signals. The DPFM measurement relies on a powerful data acquisition board and an operation principle similar to force modulation. In this case, the sample’s position was modulated at 1 kHz using a piezo-shaker, force curves were acquired for each pixel of the images. Algorithms, which can be used in real time or post acquisition, can define a number of sample characteristics such as stiffness, adhesion (see www.witec.de for details).

B. Characterisations

Contact angle studies were performed with a sessile drop instrument (Cam 200 optical contact angle meter by KSV Instruments) using 3 micro-liters drop of distilled water. Raman analysis was carried out with a LabRam confocal microscope with 633 nm excitation using a 50x objective, confining the analysis to a few micron spot size. SEM analysis were performed with two instruments; a Hitachi S2000N with good low kV operation and a FEI Quanta 3D dual beam system. In most case, the SEM imaging was conducted at 20kV with secondary electron (SE) detection. The Quanta 3D system also operated as a focused ion beam (Liquid ion source, operated here at 30 kV, 1-10 pA), called hereafter scanning ion microscope (SIM). AFM studies were done with a Veeco Dimension 3100 system with a controller IV (used in contact and tapping mode) using a variety of Si monobeam levers (TESP; 40N/m for tapping, FESP; 3N/m for force modulation measurement and Budget sensor 0.3N/m for contact mode). Unless specified otherwise, the AFM images presented here are obtained in tapping mode with the TESP lever, near resonance, at the highest possible set point (gentle tapping regime) with 512 pixels and 1 Hz scan rate. Since most of the expected NSL features are submicron in size, and as for any extensive AFM study, tip wear cannot be completely ignored, we used a blind reconstruction algorithm (SPIP software from Image metrology S/A.) to extract the possible effect of tip convolution. Mostly, we found little difference between the raw and de-convoluted images. We also used specific AFM techniques to track differences in surface properties such as stiffness and adhesion, firstly using the lift-mode/interleave option of the Veeco software, secondly using digital pulse force mode (DPFM) from Witec Gmbh. In the Veeco interleave lift mode one AFM line is scanned in the normal manner, the next line is scanned with the feedback off, at a preset height above the surface and using the topographic information from the previous line to “follow” the surface, displaying either phase or amplitude signals. The DPFM measurement relies on a powerful data acquisition board and an operation principle similar to force modulation. In this case, the sample’s position was modulated at 1 kHz using a piezo-shaker, force curves were acquired for each pixel of the images. Algorithms, which can be used in real time or post acquisition, can define a number of sample characteristics such as stiffness, adhesion (see www.witec.de for details).

III. RESULTS

Piranha solution removes organic contamination from the surface but also makes the Si surface hydrophilic, hence helping in spreading the aqueous colloidal suspension over a larger area. This allows the nanospheres to nucleate at the periphery of the meniscus rapidly. We found that the as received, acetone cleaned and piranha treated Si substrates have contact angle of, respectively, 56.6±1.2°, 68.9±0.5° and 21.0±2.3°. Clearly, the piranha treatment makes the Si surface super-hydrophilic although the standard deviation is larger in this case.

Indeed, this piranha treatment gave the best nanosphere coverage (larger defect-free areas). Some example are shown in Fig. 1 (1(a) SEM and 1(b) AFM). The packing is clearly 2D hexagonal close-pack with a number of single (vacancy) and line defects. This method resulted in relatively well ordered area in excess of 20,000 μm². Typically, the 20 μl of nanosphere suspension spreads over an approximately circular area (6-9 mm diameter) covering most of the square 1cm² Si substrate. This defined a “coffee-drop”, henceforth called the boundary layer, where multilayer PS material is found. On each side of this boundary are regions of high order, as discussed above. These regions are specifically located on the bottom side of the substrate (with respect to the 4° tilt angle), and especially directly outside the boundary region. One should note that this was obtained without the use of surfactant which is an advantage; Surfactants tend to make an intermediate layer between the nanosphere and
TABLE I: Dimensions of the features observed for NSL preparation with magnetron sputtered cobalt films. Metrological measurements of the various features (in nm), measured mostly with AFM, in some cases with SEM (indicated in bracket with a “*”). Dimension for the various features are average diameter (ring), diameter (circle, cups), and apex-base length (triangle).

| Features          | Spacing   | Height     | Dimension          |
|-------------------|-----------|------------|--------------------|
| Triangles         | 304.5±1.5 | 9.6±3.7    | 268.5±17 (*125±20) |
| Rings             | 517±3     | 10.2±1.7   | 160±20             |
| Circle            | 517±7     | 24±6       | 350±10             |
| Cups              | (*483±8)  | (*250±14)  | (*483±8)           |
| Rings from heating| 506±4     | 28±4       | 265±10             |

silicon which could perturb the metal deposition.

SEM analysis of the cobalt deposited samples indicate no change in nanosphere arrangement, the close-packing was conserved. There is also no decrease of sphere diameter, which could result from plasma etching. Once the samples are toluene treated, a number of features can be seen on their surfaces, the main characteristics are gathered in Table I. In Fig. 2 we show SEM and AFM images of the expected triangular features for single layer 2D hexagonal close-packing. The triangles are larger on the AFM images; the triangular apex-base length is 125±20 nm for the SEM and 268.5±17 nm for the AFM image (theoretically 116 nm). However, both instruments give similar inter-triangle distances of 304.5±1.5 nm, in good agreement with the theoretical values (288 nm). The triangular apex-base length is 125±20 nm for the SEM and 268.5±17 nm for the AFM image (theoretically 116 nm). The feature height in the AFM image is around 9.6±3.7 nm. One should note, however that where wide line defects were present, the thickness of these cobalt zigzag stripes was much thicker (up to 60 nm). In general, these well ordered hexagonal arrays of triangular features are situated around the coffee-drop boundary, in the same regions shown in Fig. 1.

Figure 3 shows another region where the triangles had a central circular feature situated at the center of each hexagonal cell. Although the triangles are bright (high SE signal) and “between” the nanospheres, these central circular features are dark (low SE signal) and “under” the spheres. Nonetheless, the AFM image shows that these features are raised, although very shallow (~5 nm). They have approximately the same diameter in the SEM and AFM images. SPIP image deconvolution shows a very slight tip broadening which clearly indicates that these features are full, and not hollow like the rings.

In a few restricted area of the sample, we found features resulting from a square arrangement of nanospheres, as shown in Fig. 4. These were generally found at the boundary of hexagonal single layer regions. This cubic orderings have also been observed by others [18, 19].

Figure 5 show another area where ring-like features are observed. These rings are positioned “under” the spheres (like the circles), have approximate diameter of 160 nm and are raised (10nm high from the AFM image, Fig. 5(b)and Table I). With respect to the surrounding materials, these rings are dark in the SEM (Fig. 5(a)) and bright in the SIM images (Fig. 5(c)), as long as the beam current is low and the exposure short, otherwise etching and charging are likely to change the contrast of the SIM image. As for the triangular and central circular features, these rings are in the vicinity of the boundary layer, generally adjacent to a well ordered area showing standard triangular features. In some cases, the rings were linked by straight rod-like segments (Fig. 6(a)), a surprising result which we can not explain at present. As a mask to deposition, the spheres could not produce such straight features. Furthermore, we found out that these features are unlikely to be a characteristic of the deposition pro-
over several periodicity. These egg-boxes, cup-like structures extend under the spheres with a 500 nm area positioned either within a cup region or a Co coated Si region are shown in Fig. 7(b); clearly the cup’s composition is mainly C and O, very little CoL signal is detected. Figure 8 also show Raman analysis of these cup regions, compared to a similar analysis done on the PS nanosphere single layer array (prior to cobalt deposition). In both spectra we can recognise Raman vibrations representative of polymeric bonding environments found in polystyrene with however notable differences. The C-H stretch wave number region (~2900 cm⁻¹) lacks the higher wave number component characteristic of C-H bonds attached to aromatic rings,

the C=C ring modes around 1600 cm⁻¹ are missing in the cup spectrum. Finally, there are some additional low wave number peaks (825, 671 cm⁻¹) in this cup spectrum. These results would tend to indicate that the cups are indeed polymeric but that the phenyl ring has been modified with respect to the pristine nanosphere regions.

### IV. DISCUSSION

Figure 1 indicates that we obtained large areas of close-packed nanospheres. The process leading to such highly ordered assembly has been extensively analysed in the literature [20] and can be summarised as follows. The nanospheres are negatively charged to prevent aggregation in solution by Van der Waals attraction. When the suspension is dropped onto the substrate, the evaporation will bring large change of nanosphere concentration near the contact line of the drop, this concentration gradient resulting in a nanosphere flow towards this contact line. To obtain defect-free monolayer coverage the two processes must proceed at the same pace and this is generally difficult to achieve over large areas. As long as the suspension is not completely dried out, the water acts as a lubricant and the nanospheres are free to move and react to the various interacting forces; these are electrostatic repulsion between the spheres, meniscus capillary attraction between the spheres, and sphere/surface forces. Surface defects will acts as traps where the first immobilised spheres will form nuclease from which the arrangement will grow. They will also disturb the ordering as these defects are randomly positioned and will result in competing crystals growing towards each other hence defining dislocations (see Fig. 1(a)). The regularity of the arrangement will also be defined by the dynamics of crystal growth. Generally a slow velocity of growth is essential to obtain few defects, in this case this means that the evaporation rate must be slow. This is why the well ordered regions are generally found around the boundary layer, at the bottom edge of the substrate where the large contact angle slows down the evaporation rate, especially on the external edge where the tilt further increases the contact angle.

As this investigation indicates that various type of nanostructures are present on the samples, and since these are observed by a number of microscopic techniques, it is
important to not solely identify those features by looking at their shapes but to rigorously map out samples areas large enough to include recognisable defect zones and therefore insuring that, the two compared techniques are looking precisely at the same area. This is generally a lengthy process of acquiring images at various magnifications with identifiable markers (boundary region, Si edge, particular defects, etc.) however it gives real and unambiguous comparisons. An example is shown in Fig. 9 where SEM and AFM images of the same area are shown.

Looking now at each individual features in turn; we find that the dimensions of the triangles measured by SEM (Fig. 2(a)) are larger than those expected from the theory of single layer deposition. This could be due to the off-axis deposition which is known to happen in plasma deposition system, another factor could be the negatively charged spheres which attract the Co\(^{+}\) ions near their underside, hence again broadening the triangles. We also find that the AFM triangles (Fig. 2(b)) are generally larger than those measured by SEM. This can be explained by the difference in surface sensitivity and contrast mechanisms for the two techniques. Gentle tapping AFM senses topography with extreme (nm) surface sensitivity, unless specific scheme are employed it does not sense composition. The SEM secondary electron signal is largely dependent on the sample’s atomic number, and is much less surface sensitive (10-20 nm for 20 kV energy), hence will sense the Co/Si or Co/polymer interfaces. These differences may indicate that the triangular features seen in the AFM image are not exclusively composed of cobalt but also contains an organic adsorbate.

The square arrangement seen in Fig. 4 has been discussed by others [21]. Generally, the proposed mechanism is a competition between thermodynamics, which tend to minimise free volume, hence give a hexagonal packing and the geometric confinement of water between the nanospheres, which favourite’s water entrapment and the resulting cubic arrangement for the case of bilayers, quadruple layers, etc.

The ring-like structures shown in Fig. 5 have been observed by others. Giersig used angle resolved NSL and substrate rotation to produced symmetrical ring structures [11]. In our case, the absence of rotation would produce an asymmetrical ring, which we do not observe. Moreover, as discussed earlier, the plasma is very likely to be homogeneous, both in flux an angular value over the very small area (few 100 \(\mu m^2\)) where both triangular and ring structures appear. Hence the angle is not the determining parameter for ring formation. Another mechanism is off-axis deposition and line of sight plasma etching, as proposed for the pulsed laser deposition of zirconium titanate nanoring using NSL lithography [22]. This also cannot produce the feature we observe as we noted.

![SEM image and EDX spectra at 5 kV for the cups (line spectrum) and the Co coated regions (full spectrum).](http://www.sssj.org/ejssnt)
no change in nanosphere diameter after exposure to the plasma. In other studies [23, 24], the authors invoke high kinetic energy off axis ions bouncing off the substrate and the underside of the nanosphere to finally deposit a ring of metal around the bottom of each nanosphere. Again, this does not correspond to the observed features; the rings appear either without triangles or as recessed areas surrounding a raised central circle. Another clue which invalidates those mechanisms can be gained by comparing the SEM (Fig. 5(a)) and SIM (Fig. 5(c)) contrasts for the raised rings without triangular features; they are dark in the SEM and bright in the SIM. These contrast inversions are well known to microsopists. Going from low atomic number ($Z_C = 6$) to high atomic number ($Z_{Co} = 27$), the SE yield increases for SEM excitation whereas it decreases for SIM excitation, in both case by approximately an order of magnitude [25]. This is consistent with the rings observed in Fig. 5(a) and 5(c) being organic, and not deposited cobalt. One study [26] indeed shows how the adsorbed capillary meniscus around polystyrene nanospheres can lead to hexagonal arrays of ring features, a process termed evaporative staining. In the present case, we found that the plasma deposition gave temperature excursion up to 45°C Celsius. This could provide thermal activation for similar processes such as surface contaminant gathering under the spheres or the leaching of low molecular weight compounds from the spheres. The same mechanisms can be invoked to explain the formation of the central circular features found in Fig. 3.

To investigate this further we used the DPFM option to obtain stiffness images of the ring regions, shown in Fig. 10. The height image (Fig. 10(a)) is obtained in contact mode (maximal force= 100 nN), the stiffness image (Fig. 10(b)) clearly shows lower stiffness on the circles, indicative of a softer material and higher stiffness everywhere else; on the background, presumably Si, and on the large height feature seen at the bottom of the image, presumably Cobalt. For a tip radius of 10 nm, this 3N/m lever would detect very little deformation for stiff materials such as Si or Cobalt ($E > 50$ GPa, $S$ ∼ few 100 N/m, deformation ∼ few 0.1 nm) but much more for a polymeric material ($E$ ∼ few GPa, $S$ ∼ few 10 N/m, deformation ∼ few nm). Hence Fig. 10(b) suggests that
these central circular features are made of a softer material; i.e. a polymeric material. Another mean to test the surface properties of the feature is to use the lift mode interleave option, as shown in Fig. 11. Here the imaging is carried out in tapping mode (Fig. 11(a)), with low free amplitude and high set point (80% amplitude tapping, i.e. 18 nm amplitude); conditions where there is no hysteretic or hard tapping artefacts [27], suggesting an imaging that is mostly topographic. The height image (Fig. 11(a)) of this main scan is similar to that obtain in Fig. 5(b). The phase image of the main scan (Fig. 11(b)) shows high contrast on high surface slope region; i.e. where the feedback error leads to large energetic desorption (phase) due to the repulsive interaction. The main scan amplitude image, not shown here, behaves in a similar manner. Calibration of the lever indicates that the base of the lever is 9 nm from the surface during imaging. During the interleave scan, the lever is lifted by +5 nm and the oscillation is decreased to 9 nm amplitude. As the lever is now 14 nm from the surface, it is now in the non contact regime and the phase and amplitude signals measured in Figs. 11(c) and (d) are necessarily from long range interactions. The rings, therefore, give a compositional contrast with respect to the surrounding material. A final experiment was carried out to investigate if heating the nanosphere templates in vacuum could results in similar ring features. This was done using the substrate heater of the magnetron sputtering system and again temperature sensitive labels to monitor the temperature on the sample (heated up to 45°C Celsius). The sample was then toluene treated to remove the nanospheres. Figure 12 shows a SEM and AFM micrographs of this sample, clearly the same ring features are seen, including triangles, from the standard 2D hexagonal close-packed arrangement and others such as rings, circles and cups. Growth mechanisms for these non-standard features are discussed. We note the importance of off-axis deposition for magnetron sputtering and of thermally activated nano-stain formation. The comparison of results from a number of key microscopic techniques is essential to establish the nature of such small and shallow features. In the present, we can ascertain that some of these ordered nanostructures are non metallic.

V. CONCLUSIONS

In this paper we present a microscopic analysis of metallic templates prepared by nanosphere lithography. Contact angle measurements were used to optimize the colloidal dispersion onto surface-treated Si substrates. A number of features are seen, including triangles, from the standard 2D hexagonal close-packed arrangement and others such as rings, circles and cups. Growth mechanisms for these non-standard features are discussed. We note the importance of off-axis deposition for magnetron sputtering and of thermally activated nano-stain formation. The comparison of results from a number of key microscopic techniques is essential to establish the nature of such small and shallow features. In the present, we can ascertain that some of these ordered nanostructures are non metallic.

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