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Plasma modification of nanosphere lithography masks made of polystyrene beads

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Nanosphere lithography (NSL) masks consisting of mono- or double-layers of polystyrene (PS) nano-beads are fabricated on silicon exploiting the self-organization of PS particles during the controlled drying of a colloidal suspension on a surface. The shape changes and shrinkage of PS sphere masks upon treatment in an air plasma are studied as a function of initial sphere size, plasma power and treatment time. The influence of several experimental parameters, including the plasma induced temperature rise, are analysed using scanning and transmission electron microscopy. It is demonstrated that a variety of new intriguing nanopatterns can be generated on silicon surfaces by the combination of NSL and plasma techniques, largely broadening the variety of patterns available so far by NSL.

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1. Introduction

Nanosphere lithography (NSL) is a materials general, versatile and inexpensive technique to form periodic nanostructures on surfaces [1,2]. It is based on the self-organized arrangement of nanospheres from a colloidal suspension typically in a hexagonally close-packed mono- or double-layer on a solid surface. In between each triple of colloidal beads of a layer an empty space is formed, which can be used as a mask opening to deposit material in a small area on the substrate. Thus, after removing the nanosphere mask one obtains an array of nanodots, the footprint of which is either a concave triangle or hexagon, depending on whether a mono- or double-layer of beads is used. The dot height and the dot shape in the vertical direction depend on the amount of material deposited, on its chemical nature and on the deposition conditions used. While in the third dimension there is obviously some flexibility to tailor the shape of individual dots, there is apparently a strong limitation in the lateral shape of dots which can be created by NSL. In this paper we will explore possibilities to overcome these limits by subjecting NSL masks to a plasma treatment.

Often, the nanospheres used for NSL are made of either SiO_2 or polystyrene (PS). Both, SiO_2 [3] and PS [4] nanospheres have been shown to change the shape upon irradiation with keV ions due to a non-thermal, ion beam induced sintering effect at the contact points of spheres. In addition it has been shown that PS spheres tend to shrink upon ion irradiation [4] or plasma [5] treatment. The aim of the present paper is to study in detail the effect of plasma treatments on the shape of PS spheres in NSL masks.

2. Experimental

NSL masks were created by the controlled drying of a droplet of a colloidal suspension on RCA-type [6] pre-cleaned Si surfaces. For this purpose, small amounts of commercially available aqueous suspensions of PS spheres with diameters of either 200, 600 or 1000 nm were spilled on an inclined Si substrate, leading to a slowly moving droplet of suspension on the surface. Controlling the temperature and humidity in the vicinity of the droplet allows to control the evaporation rate of the liquid phase and to form hexagonally close packed mono- and double-layers of PS beads [7]. Once inspected by scanning electron microscopy (SEM) the areas of mono- or double-layer can be easily localized on a sample from the optical interference colours.

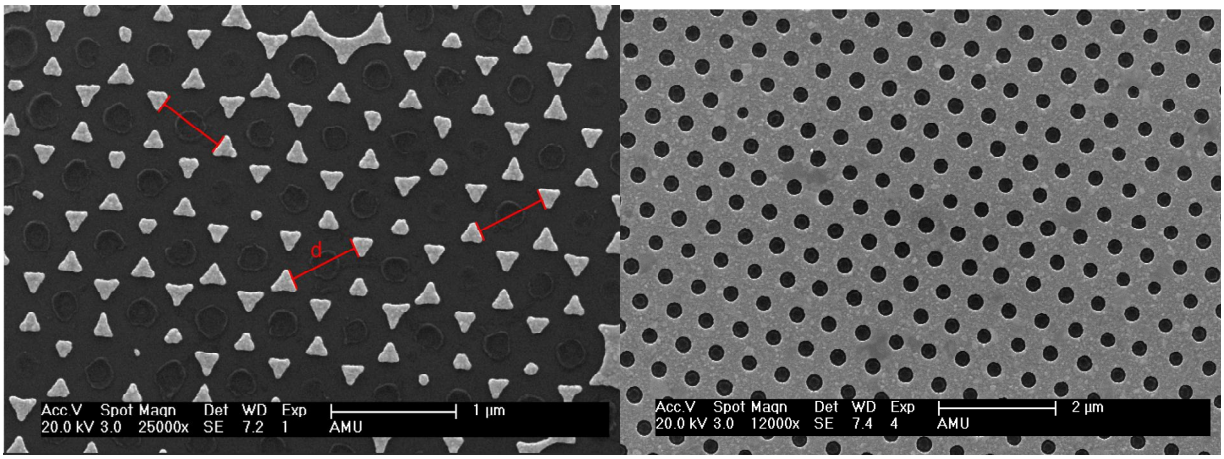
For plasma modification the samples were placed in a barrel-type plasma reactor (Plasma Prep 5, GaLa Instrumente) operating at 13.56 MHz. Unless stated otherwise, air supplied at a constant flux of 50 cm^3/min was used as plasma gas with a pressure adjusted between 40 and 100 Pa. The plasma power was systematically varied between 25 and 100 W.

Colloidal mask inspection was done with a FEI XL30 environmental SEM at 20 kV. To this end we first deposited 30 nm thick silver films by electron beam evaporation on the masks and subsequently removed the masks with adhesive tape. This procedure allowed us to record SEM images without beam charging induced mask distortions and with strong and reproducible image contrasts which – for a good statistics - could be evaluated automatically by image processing software. At the same time this procedure also reveals directly the projected

shape of nano-objects which can be formed using the plasma modified masks. Some samples were also investigated by cross-sectional transmission electron microscopy (XTEM) with a Jeol JEM 2100 FEG at 200 kV in conventional and analytical modes. For this purpose sample surfaces were covered with a cobalt protective coating prior to cross-sectional TEM specimen preparation.

3. Results

Fig. 1 shows a nanostructured Ag film on silicon using (a) an unmodified NSL monolayer mask and (b) a plasma treated monolayer mask. Using the unmodified mask (Fig. 1a) a regular array of isolated Ag dots is created, as has been observed by others before [8]. It is obvious from Fig. 1 (b) that the plasma treatment of the mask has lead to a strong shrinkage of PS beads which now cover the Si wafer only in the form of isolated dots and therefore allow for the creation of a hole array instead of a dot array as in Fig. 1 (a).



(a) *(b)*

Fig. 1. Ag dot array obtained using an unmodified 600 nm diameter NSL mask (a) and a 600 nm diameter mask and plasma treatment for 4 min at 100 W (b). Both images exhibit the sample with the mask removed.

Such regular hole arrays have a number of promising optical properties [9] and therefore have been frequently fabricated using electron beam lithography or focused ion beam techniques. NSL combined with plasma etching has the advantage of being a a fast and inexpensive technique, in which the density of holes is controlled by the NSL bead size and the diameter of holes is determined by the plasma power and treatment time. However, the diameter of holes shows some fluctuation owing to the statistical nature of the plasma process and it is not clear yet how this fluctuation influences the optical properties of hole arrays.

The temporal evolution of PS NSL mask shapes is displayed in Fig. 2 for spheres with a 600 nm starting diameter and an air plasma of 50 W power. As one can see clearly necks are formed between neighbouring spheres already after a short plasma treatment.

Spheres have shrunk and are interconnected only by the necks. The chemical nature of the necks is not clear, in particular since we also find ring shaped deposits of 5-10 nm height (as measured by AFM) on the substrate underneath each sphere after mask removal, visible by SEM in Fig. 1 a. The rings can be completely removed in an oxygen plasma. It is assumed that they originate from residuals in the suspension and that these are also accumulated at the lateral contact points of spheres, initiating the neck formation. Neck formation and sphere shrinkage get stronger until finally the necks get disrupted and hexagonally shaped particles remain on the silicon surface (Fig. 2 d). These particles get round again upon a prolonged plasma treatment (Fig. 2 e), however the etching rate gets tremendously slowed down when a residual particle diameter of about 20 % of the initial value is reached.

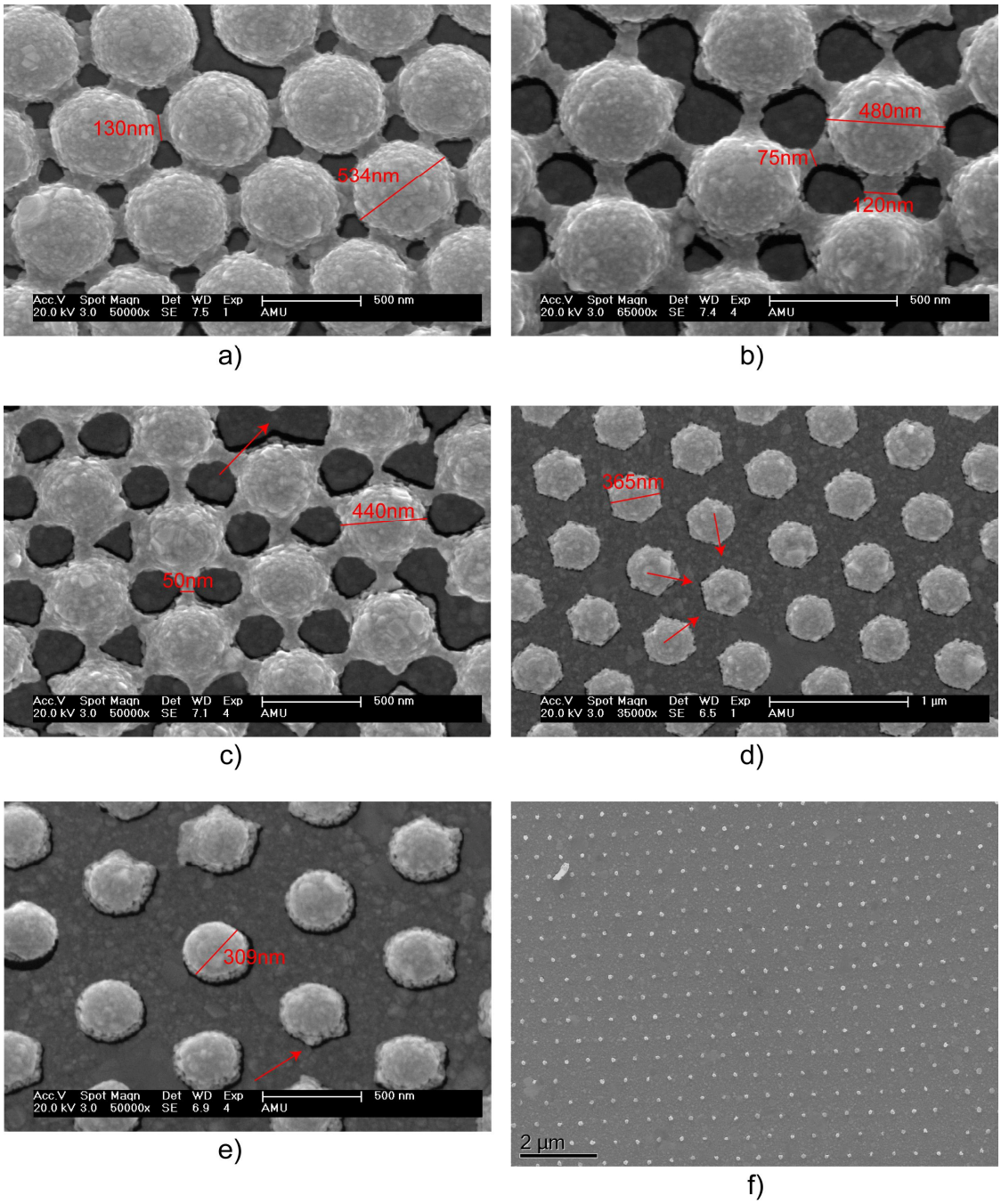


Fig. 2. SEM images of a 600 nm diameter PS bead mask treated for 3 (a), 4 (b), 5 (c), 6 (d), 7 (e) and 14 min (f) in a 50 W air plasma. The samples were covered with 30 nm Ag to improve contrasts, resulting in the grainy surface morphology.

This evolution is similar for all mask sizes (Fig. 3). In a first stage, the mask particles shrink at a small rate, followed by a stage of fast shrinkage and a final stage of slow shrinkage. Of course, the shrinkage rate is the higher the larger the plasma power is. For the small spheres (200 nm starting diameter) the first two stages seem to be shortened in duration and the final 20 % diameter is already reached after four minutes. A comparison to the particle shapes indicates that the transition from stage one (initial slow shrinkage) to stage two (rapid shrinkage) is correlated to the rupture of necks. Additional investigations (not shown) on groups of individual PS particles clearly demonstrate shadowing effects of neighbouring particles on the etch attack of beads. Therefore the necks are assumed to influence the shrinkage rate. To our surprise we observed almost

identical curves when the air plasma was replaced by an Ar plasma (not shown), most likely highlighting the dominance of physical sputtering in our reactor. Very similar curves were also obtained when the spheres were deposited on SiO_2 instead of silicon. Only for prolonged plasma treatments we then observed a slightly faster etching on Si substrates, possibly indicating some electrical charging effect leading to a retardation of the shrinkage on SiO_2.

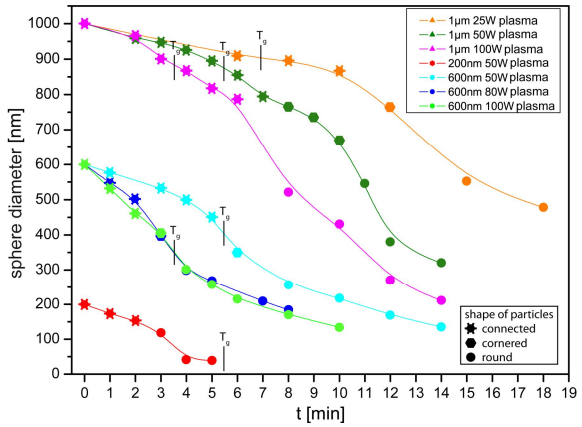


Fig. 3. Time dependence of the sphere diameter for 200, 600, and 1000 nm bead diameter NSL masks after air plasma treatment at different powers. The star-like symbols represent necked spheres, the hexagonal ones hexagonally distorted spheres and the filled circles rounded spheres.

Owing to the impact of charged and neutral particles and due to the radiation accompanying the plasma, the sample temperature rises during the plasma treatment. Using a glass mantled temperature sensor glued onto the sample and by means of temperature measurement stripes we tried to estimate the temperature evolution during the plasma treatment for the various conditions used. In particular we were interested to see when the PS glass temperature of 80 °C [10] was reached for the different plasma powers. This time is indicated in Fig. 3 by vertical lines. Obviously there is no strong correlation between the shape of curves and the glass temperature. In order to check the influence of temperature on the shape evolution of PS NSL masks directly we put masks into a furnace operated in air. Only at temperatures of 100 °C and above and for annealing times of 10 minutes and more some changes in the shape of NSL masks were detectable in the SEM. They mostly consisted in a broadening of necks and a closing of mask openings at higher temperatures and for longer times. This observation is in good agreement to results in [11] where PS mask openings were closed by heating up the masks in a fluid. It should be noted that the deformation temperature of 100 °C was reached in the plasma only after 9 min at the earliest, where all necks were already disrupted and therefore could no longer grow in width. Therefore it is concluded that the glass transition of PS has little influence on the evolution of mask shapes during the first two stages of the plasma treatment.

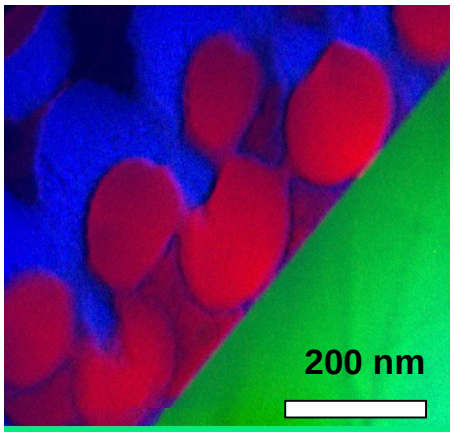


Fig. 4 Energy filtered cross-sectional TEM elemental maps of a 200 nm diameter PS double-layer mask on Si after 3 min air plasma treatment at 50 W. The sample was coated with 100 nm Co prior to s pecimen preparation. Colour code: Si=green, C=red, Co=blue.

The three-dimensional shape change in mono- and double-layer NSL masks was studied by cross-sectional TEM in conventional and energy filtered mode. Fig. 4 shows a colour coded elemental map of a double-layer of spheres after a 3 min / 50 W air plasma treatment with the Si substrate in green, carbon in red, and the Co protective layer in blue. Even though one cannot completely exclude any preparation artefacts, our studies clearly show that (a) in multi-bead layers mainly the spheres in the top layer shrink and that (b) necks form between spheres within each layer and between the spheres of different layers. The latter effect may be beneficial for the attaching of consecutive layers, while the former effect may allow for intriguing new nano-patterns, one of which is displayed in Fig. 5. Necks in the top layer of PS spheres from a double-layer mask may form a network of thin wires, interconnecting hexagonally deformed PS beads in the top layer.

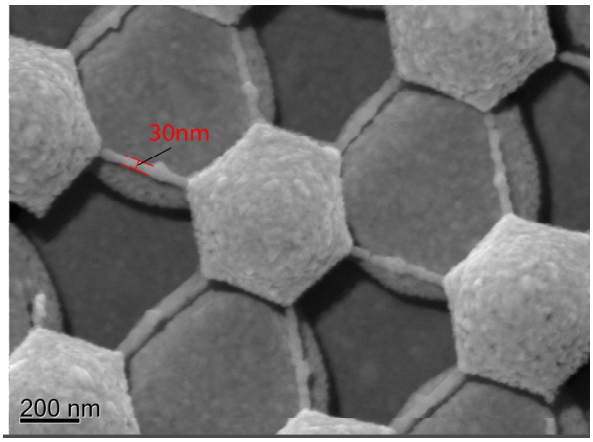


Fig. 5. SEM image of a plasma treated NSL double-layer mask made from 1000 nm diameter PS spheres. A 30 nm Ag film was deposited prior to SEM inspection.

4. Summary and conclusions

It is demonstrated that using air plasma treatments the shape of nanosphere lithography (NSL) masks made out of polystyrene (PS) beads can be significantly modified, allowing to add extra flexibility to the design of nanopatterns created by this technique. It is shown that the shrinkage of nanospheres follows a three stage temporal evolution, clearly influenced by the formation and rupture of necks between neighbouring spheres. This behaviour is similar for all NSL bead diameters (200 -1000 nm) and plasma powers used. In the final state sphere diameters saturate at about 20 % of the original size. The effect of the plasma gas species, the substrate type (semiconducting or insulator) and the plasma induced temperature rise on the shape modification are discussed. The particle arrangement is observed to influence the local etching rates, and in multi-layers of spheres mostly the top layer is modified. Thus, plasma treatment of NSL masks made of PS spheres allows to create a variety of new complex nanopatterns on solid surfaces.

References

[1] H. W. Deckmann, J. H. Dunsmuir, Appl. Phys. Lett. **41,** 377 (1982).

[2] Ch. L. Haynes, R. P. Van Duyne, J. Phys. Chem. B **105,** 5599 (2001).

[3] J. K. N. Lindner, B. Gehl, B. Stritzker, Nucl. Instr. and Meth. B **242,** 167 (2006).

[4] J. K. N. Lindner, D. Kraus, B. Stritzker, Nucl. Instr. and Meth. B **257,** 455 (2007).

[5] M. M. Silvan, M. A. Hernandez, V. T. Costa, R. J. M. Palma, J. M. M. Duart, Europhys. Lett. **76,** 690 (2006).

[6] W. Kern, in: Handbook of Semiconductor Wafer Cleaning Technology (W. Kern, ed.), Noyes Publications, New Jersey, 1993.

[7] F. Burmeister, W. Badowsky, T. Braun, S. Wieprich, J. Boneberg, P. Leiderer, Appl. Surf. Sci. **144-145**, 461 (1999).

[8] J. C. Hulteen, D. A. Treichel, M. T. Smith, M. L. Duval, T. R. Jensen, R. P. Van Duyne, J. Phys. Chem. B **103,** 3854 (1999).

[9] T. W. Ebbesen, H. J. Lezec, H. F. Ghaemi, T. Thio, P. A. Wolff, Nature **391,** 6679 (1998).

[10] L. Yan, K.Wang, J. Wu, L. Ye, J. Phys. Chem. B **110,** 11241 (2006).

[11] A. Kosiorek, W. Kandulski, H. Glaczynska, M.Giersig, small **1**, 439 (2005).

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