

## Organization of silica spherical particles into different shapes on silicon substrates

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One of the classes of materials that can be obtained via the sol-gel method are uniform sub-micron silica spherical particles. When deposited on a substrate, they typically form random patterns. In this work, we introduce a method allowing one to influence the shape of the structures created on a substrate by the silica spheres. The silica spherical particles with diameter of about 500 nm were deposited on silicon substrates using a simple process of sedimentation. Various structures, like grooves and pits, were earlier prepared by wet etching on surfaces of these silicon substrates. The process led to arranging the silica spheres within the silicon structures, reproducing the shapes of the substrates. The preliminary results are documented by the images from a scanning electron microscope (SEM). Further research on improvement of the patterns forming is under way.

Key words: *silica spherical particles; the sol-gel method; patterning*

### 1. Introduction

One of the classes of materials that can be obtained via the sol-gel method are uniform sub-micron silica spherical particles [1]. The process of producing them is simple and cheap, and they can be easily modified or doped. Due to this fact, they have found a wide range of applications. For example, uniform sub-micron silica spherical particles can be used as drug carriers [2] or, by adding silver, they gain bacteriostatic properties and can be added to textiles [3]. One of the most interesting possible applications of such particles is creation of photonic crystals [4]. The function of photonic crystals is based on periodical change of the refractive index. A three-dimensional photonic crystal can be achieved by creating a “crystal” from regularly arranged, closely packed sub-micron spheres. This has been already demonstrated [5] but the

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methods used are sophisticated and expensive. We propose another, simple and cheap method of organizing silica spherical particles into different shapes by using silicon substrate with earlier prepared structures. The possibility of creating various shapes from sub-micron spherical particles could be very useful, not only for obtaining photonic crystals.

## 2. Experimental

The uniform sub-micron silica particles were synthesized following the modified Stöber method [6]. A mixture of ethanol (EtOH), aqueous ammonia solution ( $\text{NH}_4\text{OH}$ ) and deionized water was mixed with tetraethoxysilane (TEOS). The solution was stirred in a plastic flask with a magnetic stirrer at room temperature for 1.5–2 h. Then the material was left to dry and after the evaporation of the solvent, white powder was obtained. This powder consisted of sub-micron silica spherical particles with diameter of about 500 nm. The morphology of the particles has been characterized with a transmission electron microscope (TEM).

Silicon substrates with earlier prepared various structures, like grooves and pits on their surfaces, were used. These structures were made using the standard procedure of anisotropic, wet silicon etching in KOH [7]. Before putting the silica particles on the silicon substrates, they were cleaned using the standard silicon wafer cleaning procedure. The substrates were first immersed in a hot mixture of  $\text{NH}_4\text{OH}$ , hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and deionized (DI) water (the ratio of 1:1:5), in order to remove traces of organic residues. After that, they were rinsed with deionized water. Next, a thin layer of silicon dioxide ( $\text{SiO}_2$ ) was removed by dipping in a hydrofluoric acid (HF) and DI water solution (1:50) followed by another rinsing with DI water. Then, the substrates were immersed in a mixture of hot hydrochloric acid ( $\text{HCl}_{(\text{aq.})}$ ),  $\text{H}_2\text{O}_2$ , and DI water (1:1:6). This mixture was used to remove ionic contaminants, especially metals. Finally, they were again rinsed with DI water and dried. The pictures of cleaned silicon substrates characterized with a scanning electron microscope (SEM) are shown in Fig. 1. SEM measurements of cleaned silicon substrates were performed on a scanning electron microscope Joel JSM 5800LV.

The silica spherical particles were deposited on silicon substrates using a simple process of sedimentation. They were dispersed in DI water with ultrasonic stirring and then directly applied onto the silicon substrates and left to sediment. Some of the samples were dipped in the colloid, so they were fully covered with the liquid and on some of them, a small amount of the colloid was gently dropped. The effects of this procedure were investigated using a scanning electron microscope (SEM). SEM measurements of silicon substrates with silica spheres were performed on a scanning electron microscope Hitachi S-570.

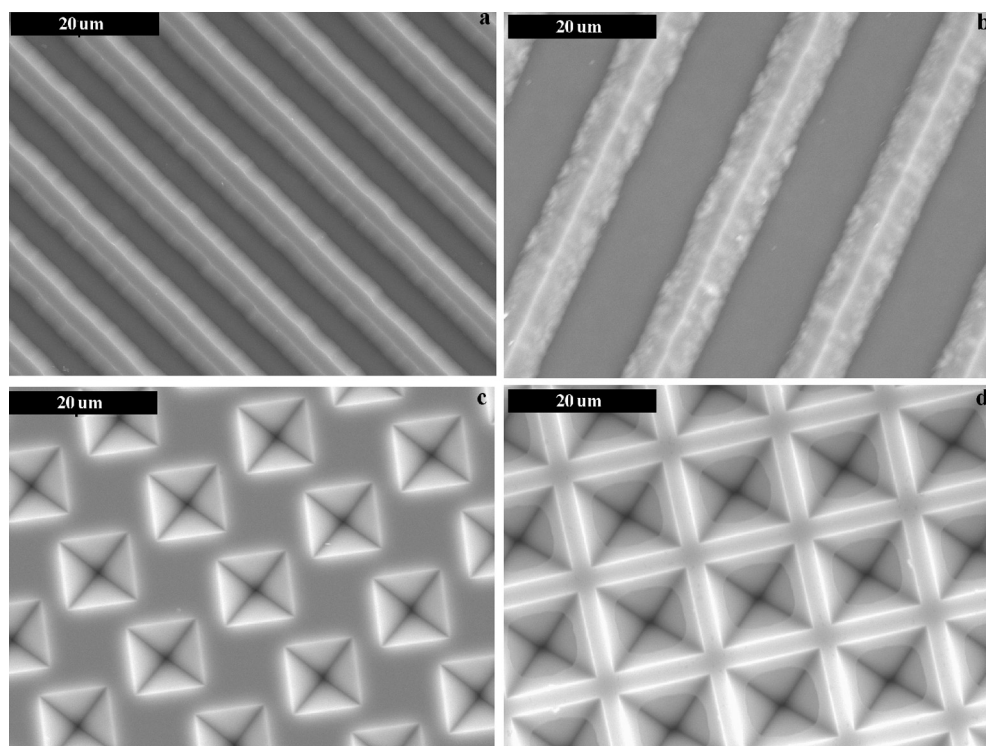


Fig. 1. SEM micrographs of the silicon substrates with etched structures: grooves (a, b) and pits (c, d)

### 3. Results and discussion

The effect of this approach was the forcing of the silica spheres to create definite patterns by arranging them in the silicon structures. It could be said that, instead of creating random patterns, they reproduced the shapes of the substrates. Figure 2 shows silica spheres within the silicon grooves. As it can be seen in Fig. 2a, all the particles are inside the structures – there are no spheres outside the grooves. Even at the ends of the grooves, the silica spheres perfectly fit within them (Fig. 2b) and there are only a few particles outside the grooves in some distance from their ends. The silica spheres on other silicon structures are shown in Fig. 3. Almost all particles are inside the pits, as in the previous case.

In the presented experiments, the amount of silica spheres on the substrates was relatively small. When the number of the particles is increasing, then, after filling up the pits or grooves, they start to fill out the space between the structures, as can be seen in Fig. 4. However, the order in their arrangement is still clearly visible. When the number of the particles is still increased they tend to create “continuous” layers on

the substrates (Fig. 5). However, even then, instead of creating random patterns, they “imaged” the distribution of the structures on the substrate surfaces.

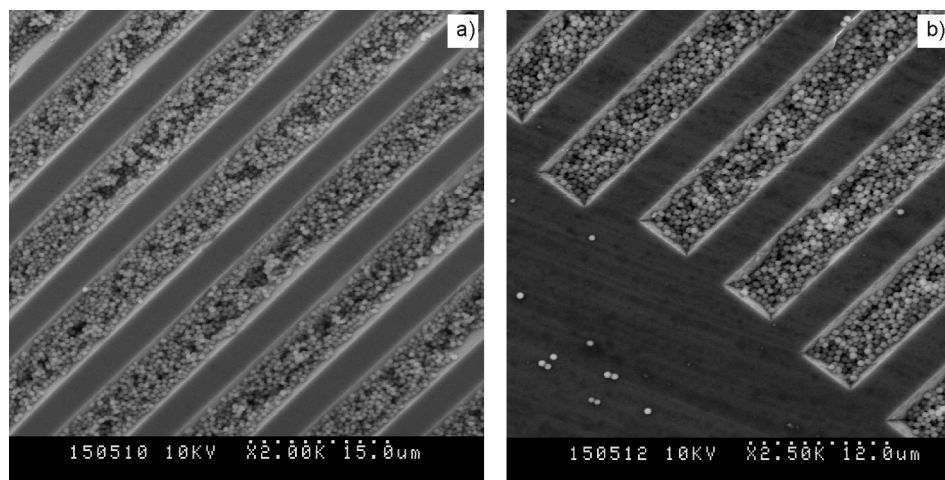


Fig. 2. SEM micrograph of the silica spherical particles within the silicon grooves;  
b) – view at the end of the grooves

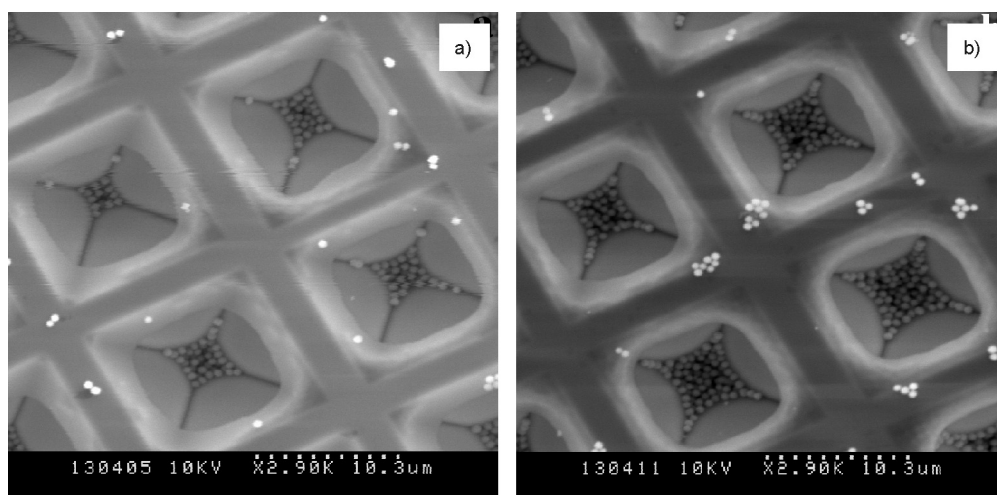


Fig. 3. SEM micrographs of the silica spherical particles  
within the silicon pits (a, b – two different samples)

As has already been mentioned, the effect of the described process strongly depends on the amount of silica spherical particles deposited on the silica surface. This of course can be controlled by the concentration of the colloid put on the samples. Another parameter which can be controlled is the amount of the colloid, which indi-

rectly defines the time of the deposition – more of the colloid means longer time needed for evaporation of the liquid. However, because of the simplicity of the sedimentation process used, the possibility to control this process is very limited. The “continuous” layer of the silica particles was obtained by using relatively large amount of the colloid with a high concentration.

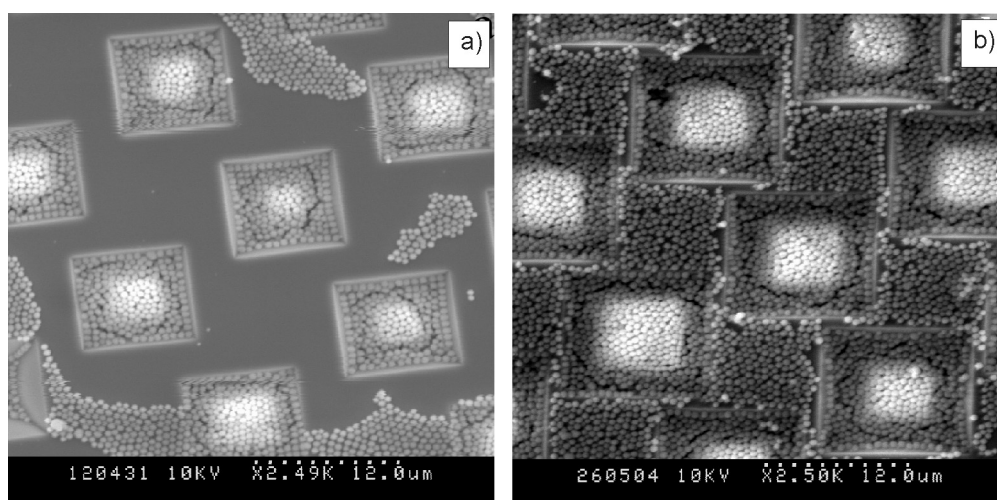


Fig. 4. SEM micrographs of the silica spherical particles within and outside of the silicon structures:  
a) smaller amount of the deposited particles, b) bigger amount of the deposited particles

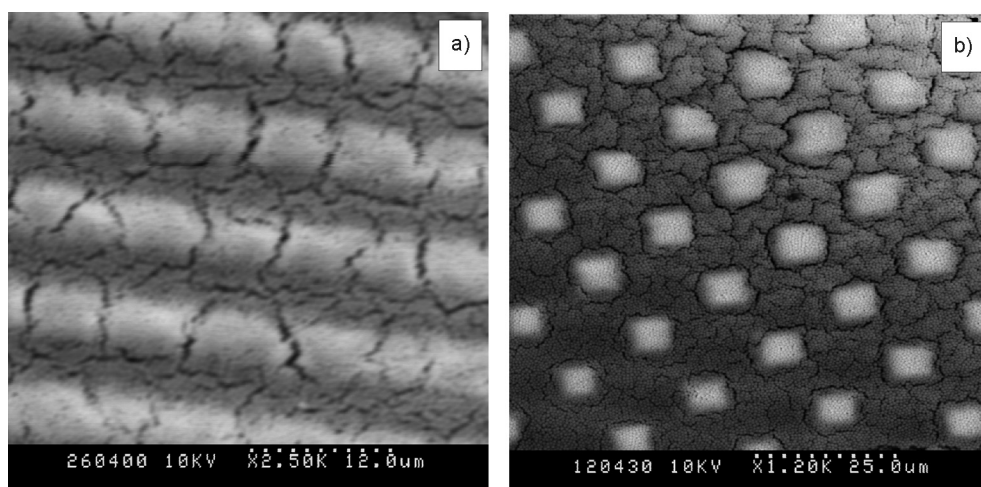


Fig. 5. SEM micrographs of the silica spherical particles creating a “continuous” layer on the silicon substrates with grooves (a) and pits (b)

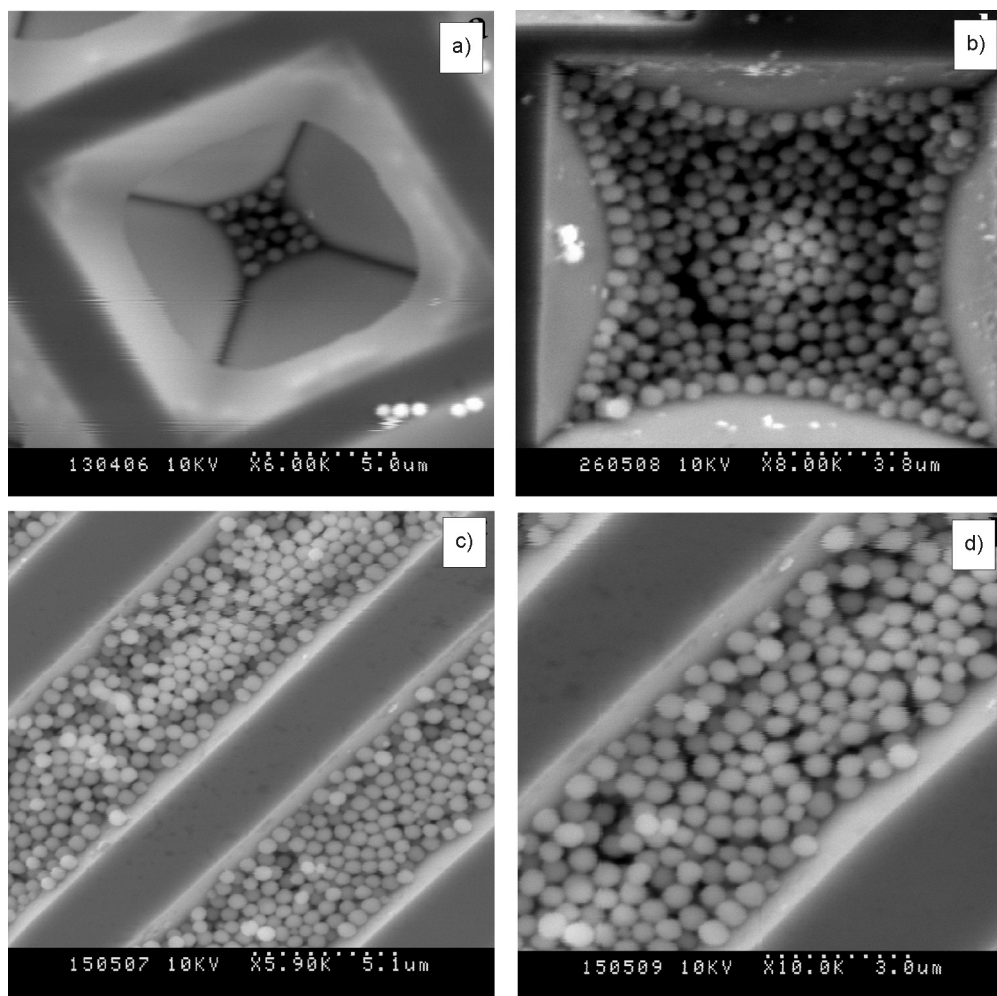


Fig. 6. SEM micrographs close-up of the silica spherical particles within silicon structures: pits (a, b) and grooves (c, d)

Figure 6 presents the close-up of the silica spherical particles inside the silica pits (Fig. 6a, b) and grooves (Fig. 6c, d). As can be seen, the arrangement of the silica spheres within the single structure is no longer so ideal. The edges of the pits and grooves limit the place for the silica particles to settle, but within the structure the positions of the spheres are more or less random. This is so because the dimensions of the silicon structures are 5–10  $\mu\text{m}$  so they are 10–20 times larger than the diameter of the silica spherical particles. The results could be improved by reducing the size of the structures. Another factor is that the silica particles have a tendency to attract each other and create larger structures. It is caused by the process of coagulation. This can

be either undesirable or desirable if the growing structures reproduced the given pattern.

It has to be mentioned that not for all the prepared samples, and in some cases not for the whole surface of the sample, we have achieved so encouraging effects. It is related to the method of deposition of silica spheres on the substrates by using the simple process of sedimentation. This could be improved by a more “active” way of deposition, for example by some mechanical shaking of the substrates or by using electrical field to organize the depositing particles.

## 4. Conclusions

We have presented a simple method of organization of silica sub-micron spherical particles into different shapes by using various silicon substrates with earlier prepared structures. The use of silicon substrates with structured surfaces and filling them with the silica spheres presents the possibility to arrange the spherical particles into various shapes. We can fill the structures with small amounts of spheres for precise arrangement or cover them with a “continuous” layer which images the distribution of the structures on the surface. The precision and resolution of the created patterns can be improved by reducing the size of the structures. The effectiveness of arranging the silica spheres can be also increased by more “active” methods of depositing them on the substrates. Further research on the improvement of pattern-forming by silica spherical particles, not only by using silicon substrates with structures, is under way.

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