

## Regular patterning of PS substrates by a self-assembled mask

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### 1 Introduction

There is a continuing interest in the exploitation of porous silicon (PS) in optics, integrated optoelectronics and in the field of microsensors. A number of recently published papers deal with ordered micro- and macro-porous structures, e.g. for lab-on-chip [1] and photonic crystal (PhC) [2] applications, etc. In order to fabricate ordered structures by anodisation a pre-patterning of the surface is needed. For the sub-micrometer region the resolution of the conventional photolithography is insufficient. Possible alternative options are electron beam lithography [3], holography [4] or fast ion beam [5] etching. High resolution patterns, however, can be achieved easily and inexpensively by means of using self-assembled nanoparticles as mask for the ion implantation [6].

The Langmuir–Blodgett technique is commonly used to prepare molecular films on solid supports [7]. Recently, it has also been successfully applied for the deposition of micro- and nanoparticulate films. The LB method enables us to transfer the structure, previously formed in a film balance at liquid-air interface, onto a solid support. The LB film can be characterized by using various techniques, e.g. optical spectroscopy, transmission (TEM) and scanning electron microscopy (SEM), atomic force microscopy (AFM), scanning tunnelling microscopy (STM), scanning angle reflectometry (SAR) and ellipsometry (SE).

Stöber's method [8] has been used for several decades to prepare silica nanoparticles in a wide size range by the controlled hydrolysis of tetraalkyl-orthosilicates [9]. These particles have several advantageous properties. They are nearly spherical in shape and have narrow size distribution; and – although they are usually porous – above a diameter of ca. 20 nm they are compact [10].

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In this work we attempt to form by means of nanosphere lithography ordered porous structures of submicrometer period for photonic crystal purposes. This film serves as a masking layer for ion implantation to generate the periodically inhomogeneous doping for the subsequent anodisation step.

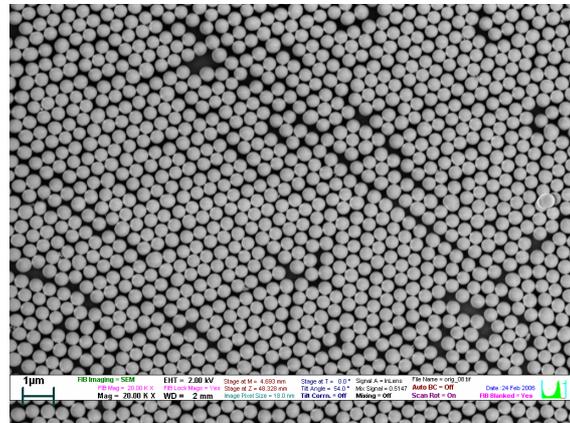
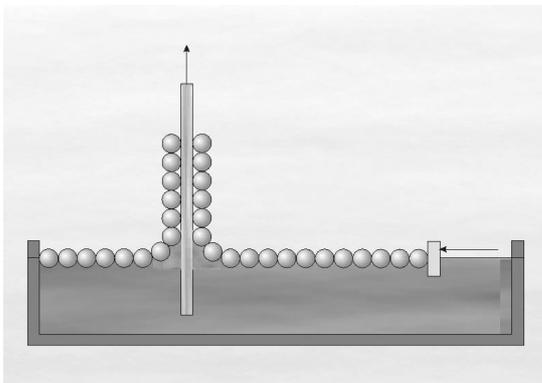
## 2 Experimental

The alcosol of the silica particles was prepared according to Stöber's method [11] by the controlled hydrolysis of tetraethyl-orthosilicate. The diameter of prepared silica particles was 350 nm, the standard deviation ca. 10% – as obtained from the TEM analysis.

For layer deposition we used  $25 \times 25 \text{ mm}^2$  rectangular pieces of silicon wafer as substrate, previously cleaned in 2% HF solution and rinsed with deionized water, absolute ethanol and, finally, dried at room temperature.

We used a laboratory-built Wilhelmy film balance for the preparation of the Langmuir films of nanoparticles. The alcosols were diluted with chloroform in a volume ratio of 1:2. Prior to spreading, the samples were homogenized for 10 minutes in an ultrasonic bath. Before spreading the particles the substrate was immersed into the water. Then the appropriate amount of the sol was spread onto the water surface in the film balance. After the evaporation of the spreading liquid (ca. 5 min) the layer was compressed with a speed of  $33 \text{ cm}^2/\text{min}$  at  $23 \pm 1^\circ\text{C}$ . The surface pressure of the layer was measured with the Wilhelmy-plate method. At ca. 80% of the collapse pressure of the sample, the immersed silicon substrate was educed from the water in vertical direction at constant surface pressure (Fig. 1), and the film was dried for 10 min under a 50 W lamp.

These mono-layered LB silica films (Fig. 2) and one double-layered sample (denominated pB2) were used as mask for the 20 keV boron and phosphorus ion implantation into (100) oriented p-type ( $10\text{--}15 \Omega\text{cm}$ ) and n-type ( $4\text{--}6 \Omega\text{cm}$ ) silicon with the dose of  $10^{14} \text{ ions/cm}^2$  (Fig. 3). For denominations see Table 1. After the ion implantation the LB silica films were removed mechanically. The thermal annealing of the implanted samples was carried out in  $\text{H}_2:\text{N}_2$  at  $600^\circ\text{C}$  for 30 min and at  $900^\circ\text{C}$  for 60 min.



**Fig. 1** Schematic representation of the fabrication of LB films.

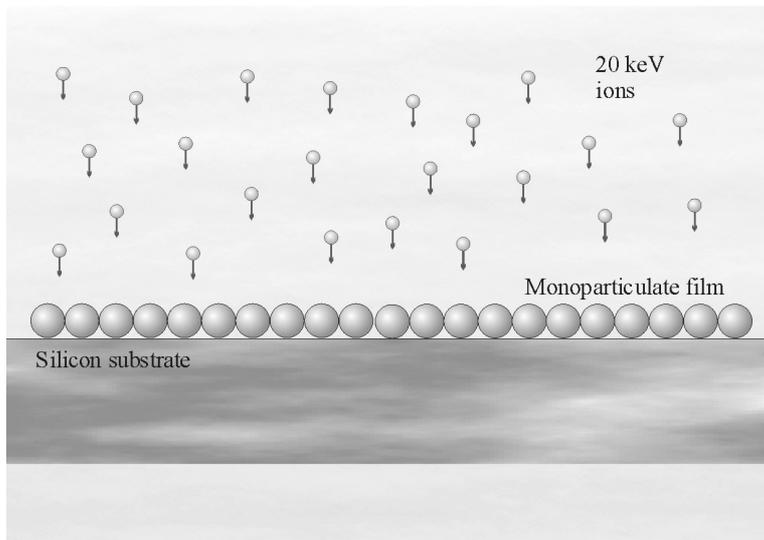
**Fig. 2** SEM image of mono-layered silica LB film used as masking layer for the ion implantation.

**Table 1** Denotation of the samples used.

Wafer	Implanted ions	
	Boron	Phosphorus
p-type	pB1, pB2	pP1
n-type	nB1	nP1

The electrochemical etching of the boron and phosphorus implanted p- and n-type silicon substrates was carried out in a 7:3 HF:ethanol electrolyte. The controlled current density was  $25 \text{ mA/cm}^2$  for each sample. The time of anodisation was selected 12 s for the p-type and 14 s for the n-type wafers. In case of boron and phosphorus implanted n-type silicon samples, the electrochemical etching was carried out with front side illumination using a 100 W halogen lamp. It is worth noting that in case of n-type wafers the silicon etching started only after the illumination was switched on. After anodisation the diffraction by the ordered porous structure was simply observable with naked eye for each sample.

Then the PS layers were removed by alkaline etching for scanning electron microscopy (SEM). The FESEM images were taken by a LEO 1540 XB microscope.



**Fig. 3** Pictorial representation of the ion implantation using nanoparticulate LB film as masking layer.

### 3 Results and discussion

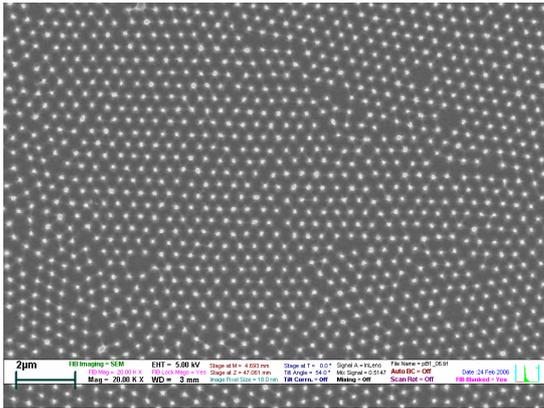
The order of magnitude of the doping density is  $10^{15} \text{ cm}^{-3}$  in the basic p-type silicon wafer with the resistivity of 10–15  $\Omega\text{cm}$  and also in the n-type wafer with the resistivity of 4–6  $\Omega\text{cm}$ . The magnitude of the doping concentration in the volume affected by the implantation is  $10^{19} \text{ cm}^{-3}$  according to Monte Carlo simulations (SRIM 2003). The thickness of the implanted layer is ca. 120 nm (ion range: 80 nm, straggle: 32 nm) in case of B implantation and ca. 50 nm (ion range: 31 nm, straggle: 14 nm) in case of P implantation. The Boron and Phosphorus ions certainly cannot penetrate the ca. 200 nm and the ca. 90 nm thick  $\text{SiO}_2$  layers, respectively.

Thereby, in case of B implanted p-type (pB1: Fig. 4, pB2: Fig. 7), P implanted n-type (nP1: Fig. 5) and B implanted n-type (nB1: Fig. 6) silicon, the samples were anodically etched preferably in the implanted regions between the nanospheres. The evidence of this can be found e.g. in Fig. 4. The crystalline silicon dots (bright spots) are missing, where a missing nanoparticle in the masking LB layer caused a nanosphere vacancy (see in Fig. 2).

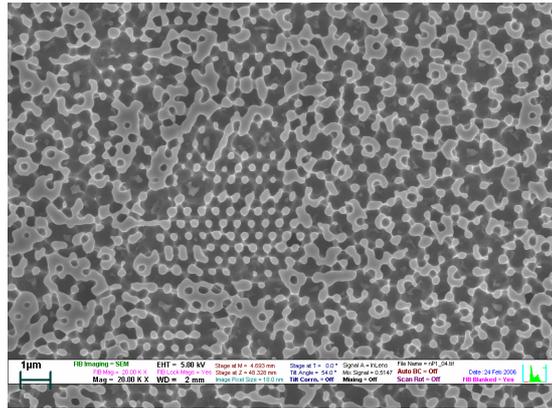
In case of the B implanted n-type sample (nB1: Fig. 6) the porous etching occurred preferably between the silica particles, where the B ion-implantation determined the type of doping. Similarly to Fig. 4 in Fig. 6: the crystalline silicon dots are missing in the matrix points, where in the masking LB layer a nanosphere vacancy was formed.

In case of the double-layer masked pB2 sample the B ions could reach the substrate only through the nearly circular windows of ca. 60 nm diameter, owing to the geometry of tetrahedral ordering of the spheres in the close packed structure. The faveolate (honeycomb-like) pore structure in Fig. 7 is the re-

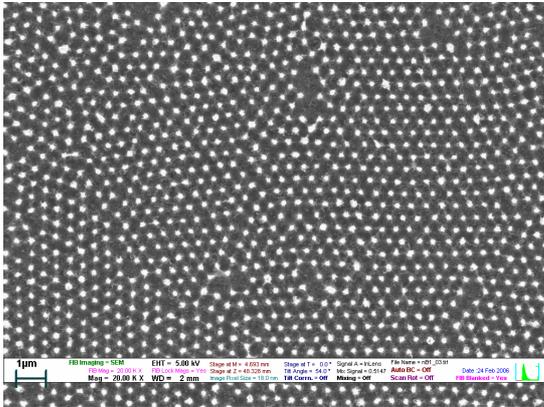
sult of the lateral extension of the porous etching from the circular implantation-doped regions during anodisation. The anodic etching stops upon depletion of the bordering region separating the porous spots from holes. This is the result of a sensitive balance between the diffusion lengths of holes and depth of the porous regions in the given substrate. These periodic patterns in an area of diameter  $> 4\mu\text{m}$  were separated by defected regions of similar size, but occurred regularly on the whole masked surface, similarly to the P implanted n-type sample in Fig 5.



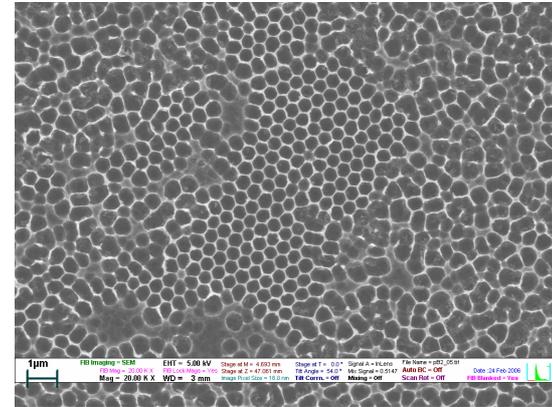
**Fig. 4** SEM image of the B implanted p-type sample (pB1) after removal of the PS layer. PS was formed preferably in the B implanted regions between the nanospheres.



**Fig. 5** SEM image of the P implanted n-type sample (nP1) after removal of the PS layer. Etching occurred preferably in the P implanted regions between the nanospheres, where the ions reached the substrate.



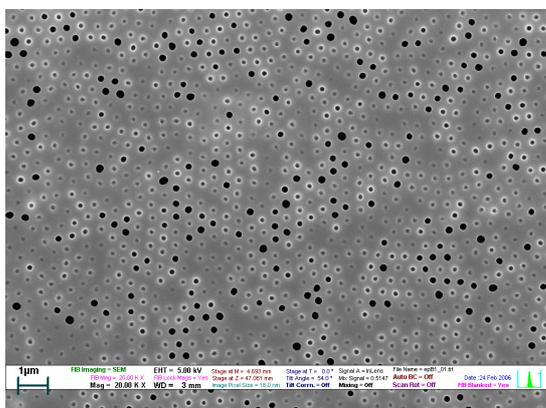
**Fig. 6** SEM image of the B implanted n-type sample (nB1) after removal of the PS layer. It was etched preferably between the masking particles, where the B ion-implantation determined the type of doping.



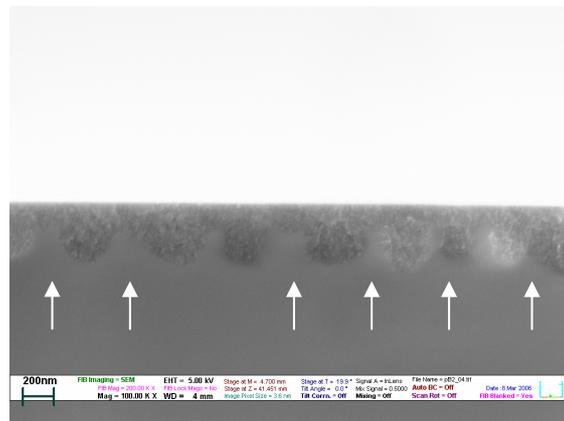
**Fig. 7** SEM image of the B implanted p-type sample, with a double-layered LB masking film (pB2). The honeycomb-like pore structure after removal of the PS layer originated from the lateral protrusion of the circular pores during anodisation.

The P implanted p-type sample (pP1: Fig. 8) was etched just underneath the nanoparticles, i.e. in the regions masked by the nanospheres. The etching front was shut in the non-implanted regions, deeper than the penetration depth of the ions it could be isotropic in several cases. These pores seem to be open. Traces of imperfections in the original LB layer can also be discovered here.

Thickness of the anodised PS layer was found to be ca. 400 nm at each sample from cross-section FESEM analysis. The ordered structure can be found also in the etched volume (Fig. 9).



**Fig. 8** SEM image of the P implanted p-type sample (pP1) after removal of the PS layer. It was etched in the non-implanted regions, i.e. masked by the nanospheres, underneath the nanoparticles.



**Fig. 9** Cross-section SEM image of the B implanted p-type sample (pB2) before removal of the PS layer. The crystalline silicon barriers in the cross-section plane are marked.

## 4 Conclusion

2D periodically ordered porous structures were fabricated in ion-implanted p- and n-type silicon. Monolayered LB films and a double-layered film from Stöber's silica spheres of 350 nm diameter were used as self-assembled masking layer in the B and P ion-implantation step. The resulting laterally periodic doping pattern was the basis for generating the various ordered porous structures by the anodic etching process. The resulting morphology was studied after removal of the PS by alkaline etching.

The B implanted p-type, B implanted n-type and P implanted n-type silicon samples were preferably etched in the implanted regions between the masking nanospheres. The evidence for this can be seen in the SEM images: the crystalline silicon pillars (dots in the plain view) are everywhere missing, where there was a nanosphere vacancy in the masking LB layer. In contrary, the P implanted p-type sample was etched underneath the masking nanoparticles.

In case of the double-layer masked B implanted p-type sample the B ions could reach the substrate only through the nearly circular windows of ca. 60 nm diameter. The honeycomb-like pore structure is originated from the lateral protrusion of the circular pores during anodisation.

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