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We propose an original approach called "stencil-masked ion implantation process" to perform a spatially localized synthesis of a limited number of Si nanoparticles (nps) within a thin SiO_2 layer. This process consists in implanting silicon ions at ultra-low energy through a stencil mask containing a periodic array of opened windows (from 50 nm to 2 µm). After the stencil removal, a thermal annealing is used to synthesize small and spherical embedded nps. AFM observations show that the stencil windows are perfectly transferred into the substrate without any clogging or blurring effect. The samples exhibit a 3 nm localized swelling of the regions rich in Si nps. Moreover, photoluminescence (PL) spectroscopy shows that due to the quantum confinement only the implanted regions containing the Si nps are emitting light.

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Synthesis of localized 2D-layers of silicon nanoparticles embedded in a SiO_2 layer by a stencil-masked ultra-low energy ion implantation process

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1 Introduction

Non-volatile flash memories based on nanoparticles (nps) are one of the promising routes to a further downscaling of future CMOS technology. The increase of scale integration should involve new features such as Coulomb blockade, quantized charging effects and single electron transfer [1, 2]. To appear at room temperature, these effects need nanometer size nps in limited number and ideally a single particle. In this context, the problem is to fabricate these nps while controlling not only their size but also their number and their position. Previous work [3] has demonstrated that a two dimensional array of Si nps embedded into a thin SiO_2 layer (from 5 to 10 nm) can be synthesized by ultra-low energy ion implantation (ULE-II) (1 keV) followed by thermal annealing (under N_2 or a slight mixture of N_2 + 1.5% O_2 at 900 to 1000 °C). At the same time, stencil mask process has been developed to transfer patterns into a selective area of a substrate either by metal deposition [4], ion beam lithography [5] or masked ion implantation [6]. Thus, the combination of ULE-II and stencil mask can be as an alternative method to locally synthesize a controlled number of self-organized nps.

In this paper, we first describe an original process, based on ULE-II through a stencil mask, to fabricate localized implanted areas of Si nps into SiO_2 layer. Observations by atomic force microscopy

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(AFM) and scanning electron microscopy (SEM), associated with photoluminescence (PL) measurements are then used to prove the efficiency of this process.

2 Stencil-masked ion implantation process

2.1 Stencil fabrication

The stencils are fabricated using a combination of deep ultraviolet (DUV) exposure and a standard micro-electromechanical processing [7]. They are made of four 500 × 500 µm membranes bored with a window array defined on a DUV resist and then transferred into the SiN layer by anisotropic etching. The thickness of these SiN membranes ranges from 200 to 500 nm. The apertures have a size varying from 220 nm to 4 µm, a pitch ranging from 1 to 10 µm and various shapes (square, circle or cross). Figure 1a shows a SEM picture of the stencil A containing rectangular micrometric patterns (5 µm long, 1.5 µm wide with a 3 µm pitch).

2.2 Nanoparticle synthesis

Prior to implantation, a 7 nm-thick silicon dioxide layer is thermally grown by dry oxidation on an 8-in. p-type (100)-oriented Si wafer. The stencil mask is then set on this substrate with a carbon adhesive tape and maintained as close as possible to the surface sample (i.e. with a very small gap). The implantation dose and the ion energy are respectively 2×10^{16} Si^+/cm^2 and 1 keV. After implantation, the stencil mask is removed and the sample is annealed for 30 minutes, at 1050 °C, under N_2 ambient. During the annealing process, the phase separation between the excess silicon and the oxide occurs and nps are formed.

2.3 Characterization of the implanted areas by SEM, AFM and PL

After annealing, the implanted areas are observed in SEM using the 'In-lens' detection of a Zeiss 1540 XB CrossBeam. Figure 1b is a SEM image of a sample implanted through the stencil A presented in Fig. 1a. It clearly shows locally implanted dark areas measuring 4.8 × 1.6 µm^2 with a 2.9 µm pitch that mimic the stencil mask used.

These observations prove that the stencil mask openings perfectly modulate the local Si dose which leads to the parallel synthesis of hundreds implanted patterns into a substrate. However, the implanted areas are slightly enlarged (less than 5%) than the stencil aperture size. This size enhancement is due to several factors such as the non-uniformity of the window sizes and the deformation of the membrane. The difference in the Si implanted dose between the centre (full dose) and the edge of a window (half dose) can also participate to these differences in size. The blurring surface (i.e. the real implanted area) depends mainly on the gap between the stencil and the sample surface (minimum here) and the ion beam divergence during ion implantation which is very small (less than 1 mrad). A gap increase for mechanical reasons might lead to an extension of the blurred area. Moreover, it can be noticed that ULE-II process does not deposit any material on the membrane sidewall which reduces the clogging effect of the

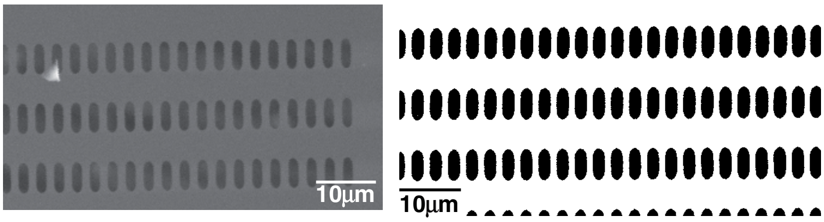


Fig. 1 a) SEM picture of a part of the periodic apertures made in the stencil A, b) SEM picture illustrating the transfer of the periodic apertures of the stencil A on the SiO_2/Si sample by Si implantation and annealing.

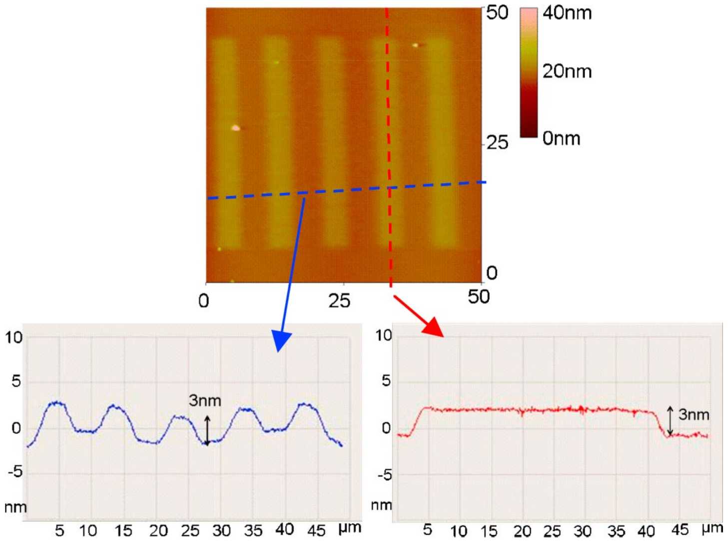
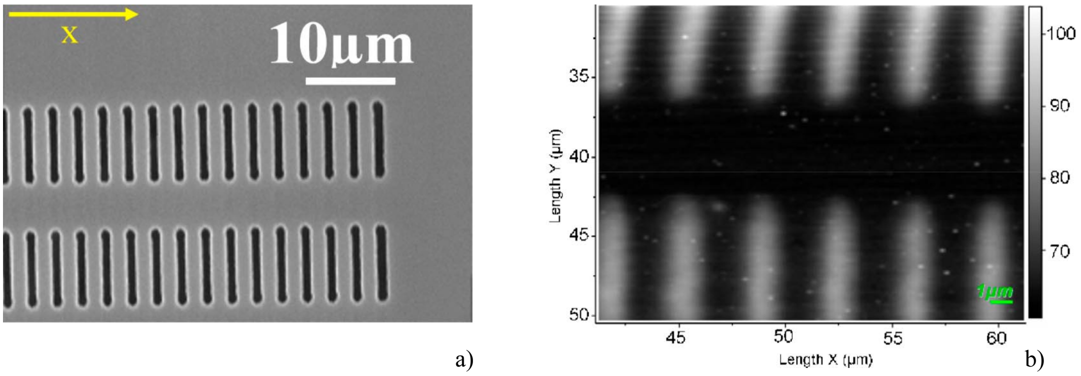


Fig. 2 (online colour at: www.pss-a.com) AFM observation of several patterns transferred on a SiO_2/Si sample after Si implantation through the stencil B and annealing.

apertures. As the dose is not too high the effect of ion sputtering is quite negligible after several cycles. Thus, this process, using ULE-II followed by annealing, leads to reduce the blurring and clogging effects, and the pattern transferred is nearly perfect in shape and size. In addition, the stencil mask can be re-used many times with no noticeable degradation.

Atomic Force Microscopy (AFM) observations in tapping mode were performed in air using a Nanoscope IIIa Multimodes from Digital Instruments to analyze the sample surface after implantation and annealing. These observations reveal that the implanted areas are clearly visible at the surface: they appear in this case as 40×5 μm^2 rectangles separated by 10 µm, which are an excellent reproduction of the windows of the stencil used for this implantation (Fig. 2). The measure of the implanted pattern thickness reveals a swelling of the oxide layer of about 3 nm, in good agreement with previous implantations without stencil in the same conditions [8]. This swelling is due to the silicon excess and partial oxidation in the matrix after implantation and annealing. The section along the length of the implanted patterns shows an excellent homogeneity of this swelling and thus of the implantation. Roughness measurements



a) b)

Fig. 3 (online colour at: www.pss-a.com) a) SEM image of a part of the periodic apertures made in the stencil C, b) PL cartography of the corresponding periodic apertures made on the SiO_2/Si sample by Si implantation through stencil C and annealing.

on the implanted zones give a mean value R_a of 0.13 nm on 40 µm, comparable to the value on the non-implanted areas.

Photoluminescence (PL) spectroscopy are performed using a Dilor XY Raman spectrometer equipped with a super notch filter used to cut the 488 nm excitation laser line, a 150 groves mm^{-1} grating and a liquid nitrogen-cooled CCD detector. The laser power at the entrance of the microscope is 150 µW or less. The incident and emitted lights are focused and collected using a confocal microscope equipped with a ×100 magnification objective working in air (0.9 Numerical Aperture).

The Fig. 3b shows a PL cartography of the sample implanted and annealed through the stencil C characterized by 9×1.5 µm^2 apertures with a 5.5 µm pitch (Fig. 3a).

For a line scan along the *x*-axis, PL measurements exhibit a succession of dark (i.e. weak PL intensity) and white (i.e. high PL intensity) zones corresponding respectively to non-implanted regions and Si implanted areas. The PL patterns measure 9×1.6 µm^2, with a 5 µm pitch. This proves that our process leads to the synthesis of localized zones of Si nps which mimic the mask geometry. The spatial evolution of nps size and oxide quality are studied by tracking the position of the peak (intensity and energy). We found that for the samples implanted through the stencil mask, the maximum PL intensity and the energy position are in good agreement with a previous study performed on implanted bare wafer [9]. A blue shift is detected on the edge of each emitting pattern which proves that the nps size is slightly larger in the centre of the implanted pattern than in the edge. This result is due to an effect of the mask edge on the implanted dose as explained before. An Energy Filtered Transmission Electron Microscopy (EFTEM) study is under progress to have more details about nps characteristics (shape, size, density).

3 Conclusion

We have presented an original technique called “stencil-masked ion implantation process” to synthesize a controlled number of Si nps by implanting silicon ions through the apertures opened in a stencil mask. SEM, AFM and PL measurements demonstrate the creation of periodic micrometric areas containing Si nps embedded into a SiO_2 layer. AFM observations show that the implanted regions induce a homogeneous 3 nm swelling of the initial SiO_2 layer. PL spectroscopy reveals a perfect matching between the detected implanted areas and the stencil mask patterns. The wavelength blue shift from the centre to the edge of a pattern shows that the Si nps are decreasing in size.

This study shows that this “stencil-masked ion implantation process” is very powerful: it allows fabricating in parallel hundreds of micrometric implanted areas with various geometries at a low-cost since the stencil mask can be re-used many times with no noticeable degradation.

Moreover, according to the nanoparticles density obtained by ultra-low energy ion implantation (from 10^{11} up to 10^{12} nps/cm^2 [10]), the 40 and 10 nm smallest achievable windows opened in the stencil mask could allow reducing to one the number of fabricated nanoparticles.

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