EFTEM studies on the localization of silicon nanocrystals embedded in SiO$_2$ for nano-devices

C. Castro$^1$, A. Andreozzi$^2$, G. BenAssayag$^1$, AM Beltran$^{1,3,4}$, G. Seguini$^2$, M. Perego$^2$ and S. Scharmm$^1$

1. nMat group, CEMES-CNRS and Université de Toulouse, 29 rue J. Marvig, 31055 Toulouse, France
2. Laboratorio MDM, IMM-CNR, Via C.Olivetti 2, 20864 Agrate Brianza (MB), Italy
3. CNRS, LAAS, 7 avenue du colonel Roche, F-31400 Toulouse, France
4. Univ de Toulouse, LAAS, F-31400 Toulouse, France

Corresponding author: celia.castro@cemes.fr
Keywords: EFTEM, non-volatile memories, self-assembled block-copolymer, e-beam evaporation, ULE-IBS.

Silicon nanocrystals (Si Ncs) based devices attract a strong interest thanks to their potential application in microelectronic and opto-electronic domains [1]. Si Ncs help to overcome downscaling limitations of the standard floating gate used in non-volatile memory devices [2-3]. In particular, the use of a multi-node charge storage provided by a Si Ncs array is beneficial to get improved retention and programming at lower voltage [4]. Because a strong correlation exists between structural characteristics and electrical properties of nanomaterials, an accurate control of the synthesis process in relation with the Ncs characteristics such as size, density and organization is necessary for their development.

2D array of Si Ncs embedded in thin SiO$_2$ layer with controlled size, density and depth have been demonstrated for different techniques like CVD [5], MBE and Ion Beam Synthesis (IBS) [6]. In particular, in the past decade, operating non-volatile memory and optoelectronic devices have been fabricated by the Ultra-low energy (ULE)-IBS followed by thermal annealing [6, 7]. Downscaling, i.e. reducing the effect of fluctuations while the number of Ncs involved in the device becomes small requires that the localization of the Ncs within the plane should be precisely controlled [8].

For this purpose, we investigated for the first time the capabilities of combining Si NCs fabrication methods like e-beam evaporation and ULE-IBS with block copolymers nanostructured masks (BC) [9]. These masks are 21 nm thick polystyrene films with a hexagonal array of vertical pores of diameter 17 nm. The mean distance between the pores is 33 nm (Fig. 1c and d) [9]. For the e-beam technique, Si or SiO are evaporated through the BC mask and after the removal of the BC, the Si dots are capped by a 10 nm SiO$_2$ layer. For ULE-IBS 1 keV Si$^+$ implantations with a fluence of $1\times10^{16}$ cm$^{-2}$ are realized through the BC mask synthesized on a 15 nm thick SiO$_2$ layer thermally grown on a (100) Si p-type wafers. In both cases a final thermal treatment under N$_2$ is added to form the Si Ncs.

Energy filtered transmission electron microscopy of the Si plasmon signal (EFTEM) was used to visualize the position of the nanoparticles within the plane they form and therefore to determine precisely their characteristics (size, morphology, density and distribution). This chemical method allows the imaging of all the Ncs independently of their crystalline state [10]. Plan-view (Fig.1a and e) and cross-section (Fig.1b) configurations were considered.

Thanks to the quantitative analysis of the filtered images, we propose to demonstrate our ability to organize Si Ncs at the nanometer level (Fig. 1e and Fig. 2). We will also show how the Si Ncs fabrication method influences the organization of the Ncs within the hexagonal array. In particular, Si and SiO e-beam evaporations will be compared. Moreover, fluence and size of the BC pores will be considered for the case of the ULE-IBS method.

The association of ULE-IBS or e-beam evaporation with BC template is a low cost and high throughput approach for in plane organisation over large areas of Si Ncs embedded in SiO$_2$ layer. Moreover, quantitative data provided by EFTEM analyses combined with other indirect analyses like electrical measurements is a powerful tool to support the development of future devices but also the validation of models [11-12].
References

[13] This research was supported by the ERANET PLUS “NanoSci-E+” consortium through the NANO-BLOCK (NANO-device fabrication using BLOCK copolymer based technology) project.

Figure 1. EFTEM images of ULE-IBS prepared samples without BC mask a) plan-view and b) cross-section and through the BC mask e) plan-view. c) SEM image of the BC mask and d) the corresponding pore diameter distribution. f) HRTEM image of crystalline nanoparticles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>No BC</th>
<th>With BC</th>
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<tbody>
<tr>
<td>Mean size (nm) ±10%</td>
<td>5.3</td>
<td>3.6</td>
</tr>
<tr>
<td>Density (nano-objects/cm³) ±20%</td>
<td>2x10¹²</td>
<td>2.6x10¹²</td>
</tr>
<tr>
<td>Coverage (%) ±40%</td>
<td>23.9</td>
<td>22.8</td>
</tr>
<tr>
<td>Mean area (nm²) ±11</td>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>±6</td>
<td>±6</td>
</tr>
<tr>
<td>Mean Roundness</td>
<td>0.6</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Figure 2. EFTEM image of a ULE-IBS prepared sample through the BC a) plan-view, b) binarisation of image a) for image analysis, c) Characteristics of the Ncs population deduced from the image analysis. Roundness = \( 4\pi \frac{\text{Area}}{\text{Perimeter}^2} \).