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Characterization of p-type Doping in Silicon Nanocrystals Embedded in SiO_2

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Materials consisting of silicon nanocrystals (Si-Ncs) embedded in silicon dioxide (SiO_2) are the subject of an intense research activity due to their potential applications for optoelectronic and photonic devices. Moreover, providing charged carriers by introducing n- or p-type dopants in these materials can drastically modify their electrical or optical properties. A plenty of studies focused on the capabilities to change the indirect bandgap of Si-Ncs to direct one and to improve the luminescence efficiency of Si-Ncs by single or co-doping. Recently a particular interest was focused on the localized surface plasmon resonance exhibited by highly doped Si-Ncs [1]. In both cases, a perfect control of the doping level and size of Si-Ncs should allow to tune the material properties. However, efficiency of these doped materials is correlated to the dopant location, which should be located in a substitutional site of the Si-Ncs. Then, it requires an accurate control of this parameter to improve and control the properties of these systems. Numerous studies concern the characterization of P doping in Si-Ncs, here, we propose to compare undoped and p-doped (with P or As) Si-Ncs by the use of Atom Probe Tomography (APT) to perform a deep structural analysis at the atomic scale. Further investigations will be done on n-type (B) doping.

Three silicon rich silicon oxide films, undoped and As or P doped, were elaborated by using ion beam synthesis process. Implantation was divided into two parts. First one consists in a ^{29}Si implantation in a $^{28}SiO_2$ 200 nm thick layer. Second one consists, for two samples, in another implantation of ^{75}As or ^{31}P chose to match with the ^{29}Si implantation range. Finally, samples were annealed at 1100°C during 4h in pure N_2 to form Si-Ncs. Structural characterization of these thin films was performed combining Time-of-Flight Secondary Ion Mass Spectrometry (Tof-SIMS) and Atom Probe Tomography. Measurements performed in Tof-SIMS allowed us to ensure the reliability of 3-D reconstruction of the tip samples.

In undoped as in As or P doped samples, Tof-SIMS revealed a region of interest, corresponding to the implantation range of ^{29}Si in the $^{28}SiO_2$ thin films, of almost 110 nm of thickness and centered at barely 55 nm from the film surface. Moreover, for As or P doping, it confirms that the implantation of ^{29}Si and both dopants species match well in the same region. We must note that considering APT composition profiles, the composition reached at the peak center of the implantation by ^{29}Si (~11 at.%) and As or P (~1.2 at.%) in each sample is almost the same. In each case, 3-D chemical maps obtained after the APT reconstruction show that the annealing treatment performed at 1100°C leads to the clustering of ^{29}Si and ^{28}Si without any distinction. The mapping of As and P atoms allowed us to highlight the aggregation of the impurities at the same position than the clustering of Si atoms. Thereby, from a first global view, both doping cases seems to be equivalent. The use of APT allowed us to perform deeper investigation on the Si-Ncs characteristics and on the dopant location. In all samples, the diameter of Si-Ncs has been measured in order to compare the size distributions of Si-Ncs. In undoped as in As doped samples, mean diameter and shape of size distribution are almost the same, but we observed strong difference of these parameters in P doped sample (figure 1.a, 1.b). In fact, for undoped and As doped samples, size distributions show a lognormal shape with a mean diameter of 2.5 ± 0.4 nm whereas for P doped sample it shows a Gaussian shape with bigger diameters (~3.3 ± 1.0 nm). Moreover, an investigation of these size distributions along the implantation profile highlighted a similar evolution of Si-Ncs diameter between undoped and As doped thin layers (figure 1.c). It allowed us to conclude that introduction of As atoms does not impact the Si-Ncs growth process whereas P atoms have strong influence on it. This may be attributed to a change of the Si diffusion length of Si atoms in presence of P atoms [2]. From a doping point of view, it has been shown that all Si-Ncs contain P or As atoms (figure 2.a). The computation of erosion profiles, which represent the evolution of species composition from the center of the Si-Ncs to the surrounding matrix, allowed us to conclude about an efficient introduction of impurities (As or P) in the core of the Si-Ncs without any pile-up of impurities at the Si/SiO_2 interfaces (figure 2.b), even for the smaller Si-Ncs for which self-purification effect could occur [3]. The impurity composition of each Si-Ncs have been computed. Its representation as a function of the Si-Nc diameter shows that both impurities follow the same tendency in term of impurity level in the Si-Ncs (figure 2.c). On one side, bigger Si-Ncs (above 3 nm), tend to stabilize at an equilibrium state corresponding to an impurity level of 5 at.%. On the other side, majority of the smallest Si-Ncs (below 2 nm) exhibits higher impurity level which can reaches values up to 45 at.%. This allowed us to highlight a size dependency of the p-doping level in Si-Ncs, and show that the formation of highly p-doped small Si-Ncs may be performed.

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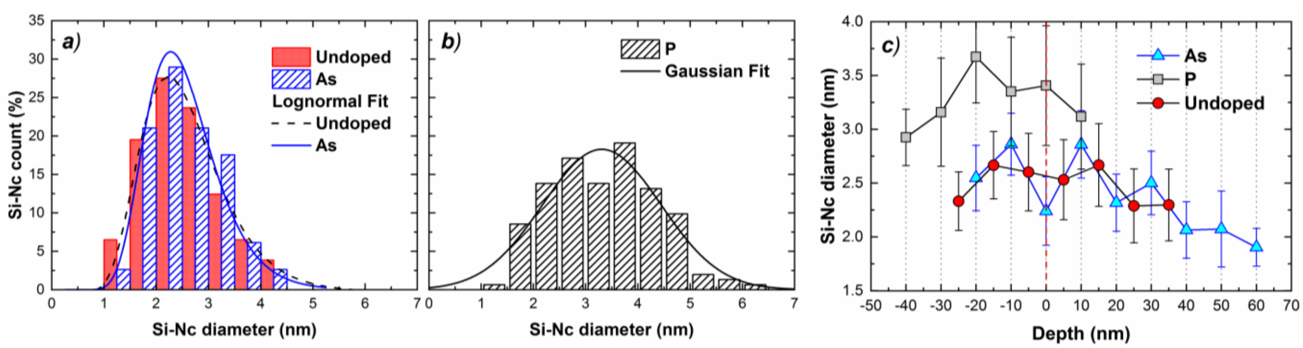

Figure 1. Size distribution of (a) undoped, As doped and (b) P doped Si-Ncs. Solid and dashed lines represent distribution fitting. (c) Diameter evolution along the implantation profile.

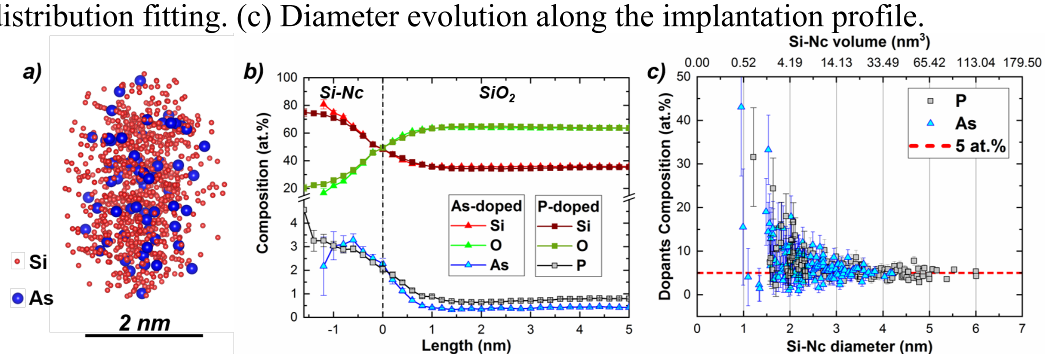

Figure 2. (a) 3-D reconstruction of As doped Si-Nc. (b) Mean erosion profile of As and P doped samples. (c) Impurity composition of each Si-Ncs as a function of their diameter.