Quantification of Phosphorus Diffusion and Incorporation in Silicon Nanocrystals Embedded in Silicon Oxide

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INTRODUCTION

The precise control of doping of nanostructured semiconductors, often referred as ‘deterministic doping’, is a key challenge for the fabrication of future advanced devices [1]. The most promising methods to solve this issue (e.g. single ion implantation, monolayer doping, etc. [2,3]) include an annealing step, where thermally activated processes such as dopant diffusion, segregation, and activation take place and need to be properly quantified for efficient device development. However, dopant quantification in nanostructures is an extremely challenging task with respect to bulk materials due to the reduced size and dimensionality and to the presence of different matrices, interfaces, etc.

Silicon nanocrystals (NCs) embedded in a SiO2 matrix can be considered as a model system to study the general problem of dopant incorporation at the nanoscale because they are the simplest and smallest semiconductor nanostructures, and can be synthesized with the highest control in their size and positioning.

However, a reliable quantification protocol for P incorporation in Si NCs has not been developed yet. In this work, following a multi-technique approach, ToF-SIMS (time of flight secondary ion mass spectrometry) has been combined with Rutherford backscattering spectrometry (RBS) and transmission electron microscopy (TEM) analyses to develop a protocol for accurate quantification of P concentration profiles both in SiO2 and in a layer containing Si NCs. To this aim, we used a particular set of samples with identical spatial and size distributions of Si NCs in SiO2 but with significantly different P profiles as a result of

RESULTS

A three-layer structure consisting of SiO2(14 nm)/SiO(6 nm)/SiO2 (10 nm)/Si has been deposited on a Si (100) substrate in an e-beam evaporation system working in high vacuum. The sample has been annealed in a conventional tubular furnace at 1150 °C for 1 h in N2 flux in order to induce Si-SiO2 phase separation and coalescence of Si NCs [4,5]. After annealing, the sample contains a single layer of well-aligned crystalline Si NCs with a diameter of 4.2 ± 0.5 nm embedded in SiO2, as shown by TEM in Fig. 1a.

Figure 1b shows the ToF-SIMS depth profiles of 31P, 30Si, 28Si2, and 28Si16O3 secondary ion intensities collected from the sample as deposited. The secondary ion yields have been normalized to the 30Si intensity. The location of the P peak, the silicon nanocrystals, the SiO2 layers, and the Si substrate have been indicated.

The experimental results have been interpreted in terms of the proportion of the phosphorus diffusion coefficient of the surface diffusion coefficient of the phosphorus atoms. The results of the present study are in agreement with the theoretical predictions of the models proposed by other authors [6,7].
$^{31}$P profile is shallower, with a peak at a depth of 22 nm, with a sharp trailing edge. P is thus entirely contained within the SiO$_2$ matrix and well separated from the NCs, with a SiO$_2$ interlayer 15 nm thick.

This starting samples where annealed at different times and temperatures: P diffuses and interacts with NCs. In particular ToF SIMS (not shown) reveals that after 900 °C 4 h all P is still within the SiO$_2$ matrix, after 1000 °C 4 h a small fraction of P (below 6% of the total integrated intensity) is trapped at the NCs, and finally after 1100 °C 4 h a significant fraction of P is trapped at the NCs. As noted previously, the quantification of the above profiles is quite challenging as P is contained in two different matrices, SiO$_2$ and Si NCs, which are expected to have quite different relative sensitivity factors (RSF).

To resolve this issue we used a technique not affected by matrix effects: RBS analyses have been performed at Laboratori Nazionali di Legnaro (LNL) in Italy by using 2-MeV 4He$^+$ beams delivered by the 2 MV AN2000 Van de Graaff accelerator. The Rutherford $^{31}$P(α,el)$^{31}$P reaction was used with a scattering angle of 165°–170° in (100) channeling conditions, in order to reduce the Si counts coming from the Si substrate. Total P dose estimations were done by fitting the RBS spectra using an appropriate simulation code considering trial P concentration profiles optimized with thickness constraints based on the P SIMS depth profiles. The P profile in all the samples is shallow enough to have reduced superposition of $^{31}$P and $^{30}$Si signals in the RBS spectra, allowing relative errors in the P dose estimation in the 6–8% range for most of the samples.

Figure 2 reports all the P doses measured by RBS as a function of the corresponding depth integrals of the $^{31}$P normalized SIMS intensity profiles of the as deposited sample (AD) and annealed samples discussed above. The graph also includes an additional data point (labeled as ‘AD#2’) relative to another sample fabricated with a similar deposition procedure.

The different symbols in Fig. 3 identify the data with respect to the different matrices where P is located, i.e. filled squares for data relative to P entirely contained in SiO$_2$, open squares for the data relative to P present both in SiO$_2$ and in Si NCs, and open triangle for the datum relative to P present only in Si NCs.

It is clear from Fig. 2 that data relative to P only in SiO$_2$ and P only in the Si NCs layer follow different trends, indicative of a significant matrix effect. The linear fit reported in the figure as a continuous line allows to estimate the RSFs’ value in SiO$_2$, whereas the RSF in the layer containing Si NCs is estimated by the single point with P only in the Si NCs (‘1100 °C + etch’). We obtain RSF of P in SiO$_2$ = 1.23±0.05x10$^{22}$cm$^3$, RSF of P in SiNCs = 6.5±0.9x10$^{21}$cm$^3$, almost a factor of 2 of difference. These coefficients allow to transform the ToF SIMS data in quantitative concentrations along the whole structure of the sample.

CONCLUSIONS

In conclusion, we developed a quantification protocol for P in the SiO$_2$ matrix with embedded Si nanocrystals by using a multitechnique approach combining ToF-SIMS, RBS, and TEM analyses, together with etching processes to isolate contributions from the different matrices. RSF values for P in SiO$_2$ and in the layer with Si NCs have been estimated, and the linearity of the P intensity in the SiO$_2$ matrix has been assessed up to 1.7 at.%. As a result high depth resolution (about 1 nm) and quantitatively chemical profile can be obtained on the nanostructure. The method opens the route for accurate study and modelling of nanoscale doping processes.