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Optical and nuclear characterization of Xe-induced nanoporosity in SiO_2

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ABSTRACT

We performed RBS, infrared (IR) and C–V measurements in order to follow the evolution of Xe, bubbles/cavities and other defects (with a focus on NBOHC: non-bridging oxygen hole center) and dielectric constant (k), in high dose Xe implantation in SiO_2. As-implanted sample provides the lowest value of k which increases with post thermal annealing. In the meantime, the concentration of negatively charged defects decreases with annealing while Xe out-diffuses after annealing at 1100 °C leaving Xe free cavities in the sample. By combining these results one can determine the contribution of nanoporosity in dielectric constant evolution.

1. Introduction

To increase the scale of integration in CMOS technology for the microelectronics industry; silicon oxide which was used for a long times in the interconnections is becoming increasingly less used because of its high dielectric constant (k) which is about 4. Under the Moore's law [1] improving the performance of these devices consists in minimizing critical dimensions and then a reduction of the dielectric constant (low-k technology).

The search for materials with low dielectric constant (low-k) showed that with the exception of doped oxides ($k<3$) [2] and purely organic polymers ($k<2.5$) [3], porous materials are potential candidates to replace silicon oxide. However, problems can arise during their integration because of their mechanical resistance [4–6]. Nevertheless, silicon oxide remains a good choice but its dielectric constant must be reduced. The best example is the use of fluorinated SiO_2 as low-k the dielectric [7]. Such a technique leads to a dielectric constant of 3.5, a value which cannot however fit with ITRS [8] requirement for present and future generation of transistors.

Our approach is based on using nanoporosity induced by rare gas implantation in SiO_2 to reduce its dielectric constant. As reported by Golden et al [9], one can reduce SiO_2 dielectric constant by introducing porosity in the sample. By keeping the porosity inside SiO_2 bulk, we can prevent our dielectric material from drawback effects arising when the porosity reaches the sample surface. Previous works [10] reported by our group demonstrated that unlike He and Ne, Kr and Xe implantation in SiO_2 results in the formation of bubbles/cavities. Their thermal evolution was however ion dependent [11].

This work investigates the effects of xenon implantation in silicon oxide. The evolution of the implanted gas is studied by the means of Rutherford backscattering RBS, while the dielectric function is extracted from both infrared spectroscopy and C–V measurements.

2. Experimental procedure

300 nm Silicon oxide was thermally grown on n-type silicon wafers. These samples were then implanted, at room temperature, with 300 KeV xenon ions at 5×10^{16} Xe/cm^2. After implantation, samples were annealed at temperatures ranging from 400 °C to 1100 °C for 1 h under nitrogen ambient.

Rutherford backscattering spectroscopy (RBS) was used to determine xenon profiles in SiO_2 along with its evolution versus annealing. RBS measurements were made at CEMHTI laboratory using 3.5 MeV Van de Graaff accelerator with 2 MeV alpha beam.

The dielectric function was determined by using the infrared spectroscopy (IR) and was also carried out at CEMHTI laboratory. Infrared spectra were recorded in the reflectivity mode. They were collected for wave numbers ranging from 20 to 5000 cm^{-1}, under a quasi-normal incidence with a Bruker IFS 113 V interferometer working under vacuum. The evolution of the new dielectric constant was deducted from the extrapolation to zero frequency of the dielectric function [12]. This later is the result of modelling the

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reflectance in a structure made of thin layer on a substrate: SiO_2 on Si in this study. A set of definitions is proposed for the construction of the model described by Songprakob et al [13]. It is important to have the reflectance spectrum of the substrate ($R_{\mathrm{substrate}}$) and the reflectance of the sample ($R_{\mathrm{SiO2/Si}}$). The reflectance of the substrate is obtained after the removal of SiO_2 layer by HF in order to study the effect of Xe implantation on substrate. In addition a low level doping (5–10 Ω cm) substrate was chosen in order to reduce the contribution of silicon substrate.

C–V measurements were performed by using a MOS capacitor and with a very high doping (10^{19} cm^{-3}) Si substrate in order to reduce its parasitic capacitance contribution. Structures were formed with thermally evaporated Al dots. Measurements were done with a 1 MHz Boonton7200 setup.

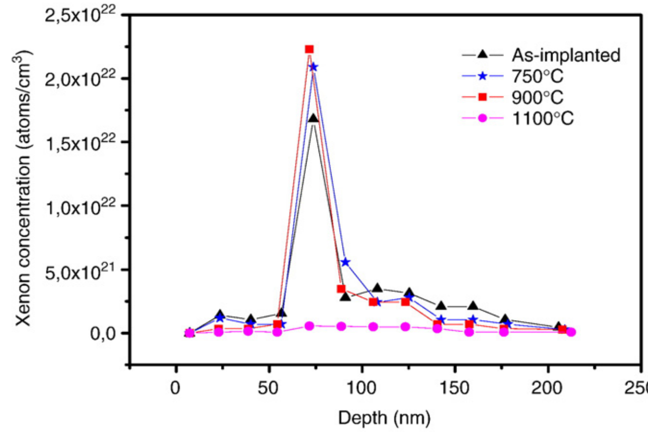

Fig. 2. Depth Profiles of implanted Xe concentration as simulated by SIMNRA code.

3. Results and discussion

3.1. Nuclear characterization

First of all it is worth to specify that studying the evolution of Xe in SiO_2 allows us to determine the actual nature of extended defects: bubbles when Xe is present and cavities which are Xe free. The experimental RBS profiles are depicted in Fig. 1 and the simulation by SIMNRA code [14] in Fig. 2 while the fraction of gas remaining in the sample as a function of temperature is presented in Fig. 3. Xe profiles exhibit a Gaussian peak with two shoulders on both sides. These shoulders tend to disappear with annealing while the magnitude of the central peak increases. Between 750 °C and 900 °C, the two shoulders disappear while the central peak reaches its maximum value. At 1100 °C Xe strongly exodiffuses from SiO_2 leaving a Xe free sample. One can speculate that Xe trapped in shoulders diffuses with annealing, toward the maximum Xe concentration peak before the total exodiffusion of Xe at 1100 °C annealing. This results in an increase of that maximum peak with temperature. We can observe that xenon remains very stable in sample until 900 °C. Such a stability is not dose dependent since many authors [11] reported the same behaviour for various dose including lower ones.

In a previous work [15] we studied the evolution of bubbles/cavities by XTEM. As shown in Fig. 4a [15], XTEM images of Xe implanted SiO_2 report the presence of nanostructures containing xenon and identified as bubbles/cavities. Measurements provided a bubble/cavity band of 120 nm in width, with a mean bubble/cavity diameter of 20 nm. At 750 °C annealing we could observe the growth of these bubbles/cavities Fig. 4b. After annealing at 1100 °C bubbles/cavities are still present in the sample (Fig. 4c).

Assaf et al [16] reported by using positron annihilation spectroscopy (PAS), that negatively charge defects (NCD) are present in samples for temperature up to 750 °C. The nature of NCD defects is most probably the NBOHC (non-bridging oxygen hole center) and/or PR (peroxide center). NCD were reported to disappear after annealing at temperatures higher than 750 °C.

From XTEM, RBS and PAS techniques we can concluded that:

- up to 750 °C: Negatively charged defects (NCD) and bubbles are present in the sample;
- from 750 °C to 900 °C:Only bubbles are present in the sample;
- at 1100 °C: only cavities are present in the sample.

3.2. IR and C–V characterization

To determine the actual value of the dielectric constant after xenon implantation, characterization were performed with IR spectroscopy and C–V measurements.

IR measurements: Fig. 5a, b, c and d shows experimental and simulated reflectance spectra of various samples including substrate (Si only), virgin (SiO_2/Si), as-implanted and annealed ones. Using FOCUS code [17], we could fit reflectance spectra of the substrate (SiO_2 was removed) and reflectance spectra of the sample (SiO_2/Si).

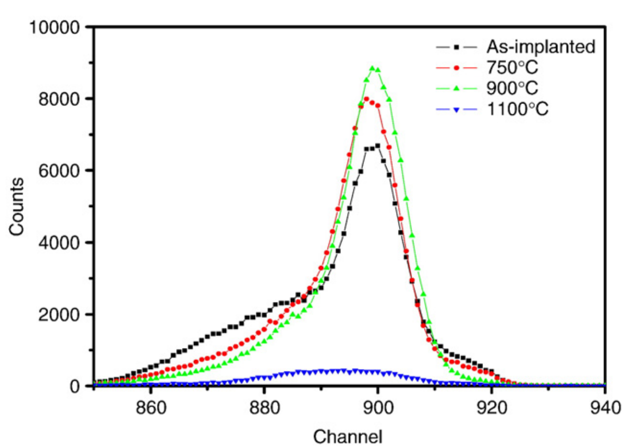

Fig. 1. Xe profiles as providing by RBS after 300 keV Xe implantation in SiO_2 with a dose of 5×10^{16}/cm^2.

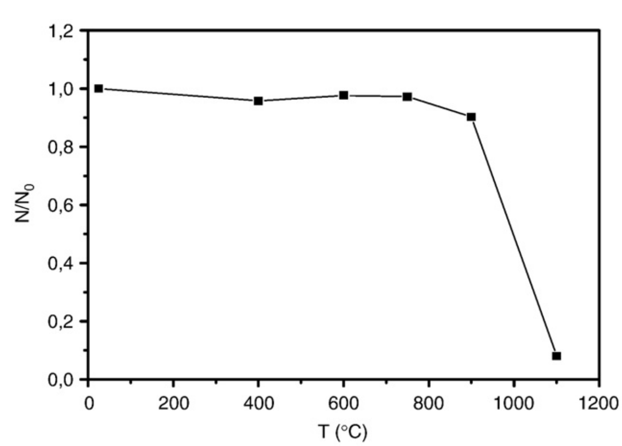

Fig. 3. Thermal evolution of Xe concentration remaining in the sample.