Materials Science and Engineering B 182 (2014) 45–51

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

Short communication

Growth and migration of nanocavities in He^+ multi-implanted Si measured by *in situ* small-angle X-ray scattering

M. Dumont[a], G. Regula[a,*], M.-V. Coulet[a], M.-F. Beaufort[b], E. Ntsoenzok[c], B. Pichaud[a]

[a] Aix-Marseille Université, CNRS UMR 7334, IM2NP, Campus de Saint-Jérôme, Avenue Escadrille Normandie Niemen-Case 261, F-13397 Marseille, France
[b] CNRS, Université de Poitiers, UPR 3346, Pprime, Boulevard Marie et Pierre Curie, Boite Postale 30179, F-86962 Futuroscope, Chasseneuil, France
[c] CNRS, Université d'Orléans, UPR 3079, CEMHTI, 3A Rue de la Férollerie, F-45071 Orléans, France

ARTICLE INFO

Article history:
Received 22 April 2013
Received in revised form 4 October 2013
Accepted 12 November 2013
Available online 7 December 2013

Keywords:
Silicon
Helium
Implantation
Growth
SAXS
TEM

ABSTRACT

Multi-implantations of He ions were performed on Si samples with (111) or (100) surface orientation in the kiloelectron volt (keV) energy range. The fluencies were chosen to keep the local He concentration constant and above the threshold to get nanocavities upon annealing. Small-angle X-ray scattering (SAXS) experiments were carried out, for the first time ever, to follow *in situ* the evolution of the size distribution of nanocavities created in the Si bulk. The cavity distribution was measured in the as-implanted state and followed during annealing from 623 K up to 973 K. The final spatial distribution was obtained *ex situ* by transmission electron microscopy (TEM). Whatever the surface orientation, the increase of the porosity is triggered at 973 K which is a temperature at least 200 K higher than expected. This ongoing increase proves that the growth stage is not complete even after a 2-h annealing. The onset of a new nanocavity population in the (111) Si sample is an experimental evidence that the migration–coalescence (MC) process, although weak at such a low temperature range, contributes to the evolution of the nanocavity size. Basic mechanisms for the growth and coarsening of nanocavities/bubbles are discussed in view of the experimental data arising from *in situ* SAXS measurements coupled with *ex situ* TEM observations.

1. Introduction

Growth and coarsening mechanisms of nanocavities in solids are of great importance for both fundamental and technological aspects [1]. For example, the understanding of cavity formation mechanisms is of major importance to predict the damages in the confinement materials in a nuclear reactor and/or to secure the storage of nuclear wastes [2]. Besides applications in the nuclear field, nanocavities are used in microelectronics and optoelectronics. They can be gettering sites for metal impurities in silicon [3,4], triggers for relaxation in Si–Ge thin film [5] and engineered defects for designing nanoparticles [6] or controlling dopant diffusion [7,8]. Nanocavities can be created within a solid as a consequence of several processes connected with ion beam or nuclear technologies. When helium is incorporated into a solid, because of its very low solubility, it segregates into small gas-vacancy complexes favouring the nucleation of bubbles, that is, gas-filled cavities with a size lower than 4 nm. When implanting helium in silicon and in contrast to the case of metals, He is not permanently enclosed in the cavities [1]. It was first suggested that an annealing at about 773 K systematically causes He to out-diffuse from the bubbles [9]. It was later demonstrated that He release strongly depends on the implantation parameters such as the He energy and dose and the implantation temperature [10]. Moreover, the annealing procedure was also shown to play an important role in the release of He: parameters such as the ramp rate [11,12], the annealing ambient [13] and the maximal temperature reached [9,14] led to significant changes in the desorption kinetics. However, whatever the He desorption state (complete, leaving nanovoids or partial, leaving bubbles in Si), this subsequent annealing causes nanocavity (He-filled or empty) coarsening with the temperature and/or time. There are still controversies on the nature of those coarsening mechanisms; either Ostwald ripening (OR) or migration–coalescence (MC) [15–17] processes are proposed. On the one hand, during OR, the smaller cavities are less stable due to curvature effect than bigger ones and, thus, in the absence of vacancy supersaturation in the solid solution, they dissolve to supply larger cavities with solute. On the other hand, the activation of the MC process is possible, thanks to the high surface/volume diffusion of individual nanocavities. This process relies on random motion of individual objects until two of them encounter one another and coalesce to form a bigger cavity. The controversy about the coarsening process mainly relies on the difficulties in bringing an experimental evidence for one of the mechanisms in favour of the other and in evaluating its importance. In spite of the numerous

* Corresponding author. Tel.: +33 491 282 756.
E-mail addresses: gabrielle.regula@univ-amu.fr, gabe.mrs@gmail.com (G. Regula).

0921-5107/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.mseb.2013.11.006

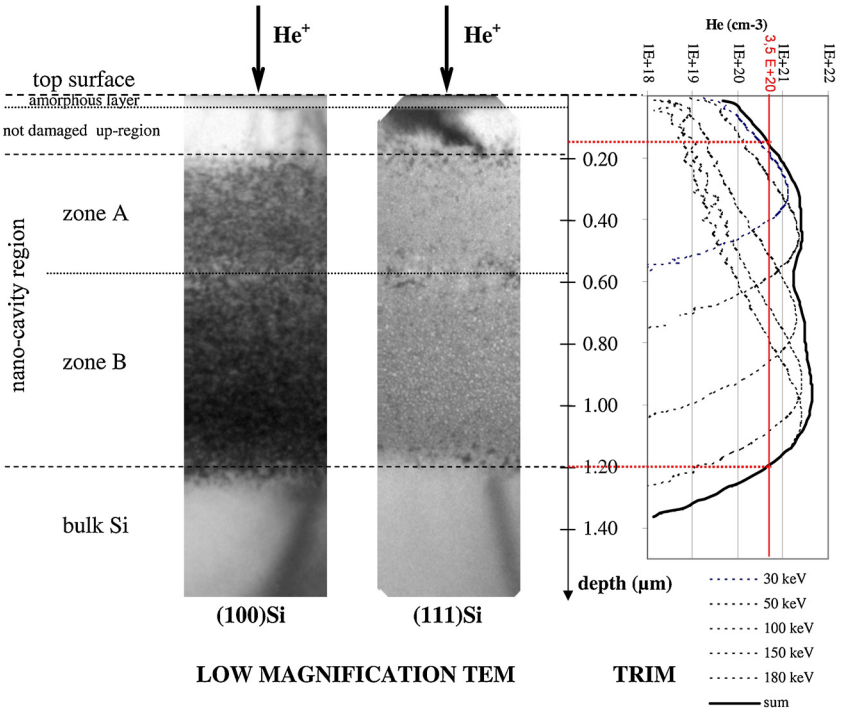

Fig. 1. Bright field TEM micrographs of as-implanted (1 0 0) Si and (1 1 1) Si in two beam conditions, $g = 0\,2\,2$ and $0\,\bar{2}\,2$, respectively and corresponding TRIM calculations given in terms of He concentration profiles for each of the five different implantations and the resulting sum.

studies on cavities in gas-implanted Si, the evolution of the mean radius of cavities as a function of time and temperature is often studied through *ex situ* observations [18,19] and only a few studies were performed during annealing [17,20]. Both mechanisms were examined from a theoretical point of view by Evans [16]. The purpose of the present work is to provide *in situ* experimental data on nanocavity size evolution kinetics in He^+ multi-implanted Si during low-temperature annealing using a quantitative *in situ* method, in a 'bulk environment', using small-angle X-ray scattering (SAXS) experiments: these data could be, in a future work, simulated using an adequate model to try to get even more information concerning the elementary process(es) involved.

He multi-implantation was chosen in order to increase the numbers of scattering objects (nanocavities) to improve the SAXS signal-to-noise ratio. Small-angle scattering techniques were shown to be a powerful technique in investigating nano-objects embedded in a matrix by giving access to their quantitative features such as their size distribution, their volume fraction and their mean radius [21], assuming they exhibit a known shape. The high flux of X-ray synchrotron radiation allows reducing the acquisition time, which makes SAXS suitable for *in situ* experiments. In this study, the evolution of nanocavities is studied during an annealing up to 973 K by *in situ* SAXS measurements combined with *ex situ* transmission electron microscopy (TEM) observations.

2. Experimental details

2.1. Materials

The multi-implantation process was performed at the physics and mechanics of materials department (DPMM) of the Pprime Institute (P′ – Poitiers – France). This multi-implantation process consists of successive He-ion implantations with different implantation energies and doses, starting with the higher implantation energy and attempting to keep the local He concentration constant, just above the threshold allowing the formation of nanobubbles. He^+ ions were implanted into Si single crystals with two kinds of surface orientations, (1 0 0) or (1 1 1). The energies and fluences ranged from 30 to 180 keV and from $2.5 \times 10^{16}\,cm^{-2}$ to $7.0 \times 10^{16}\,cm^{-2}$, for (1 0 0) and (1 1 1) orientations, respectively. In the following, these p-type samples ($[B] = 2–3 \times 10^{14}\,cm^{-3}$) are denoted (1 0 0) Si and (1 1 1) Si.

Using TRansport of Ions in Matter (TRIM) simulations, He concentration profiles were estimated and are plotted in Fig. 1. The chosen energies and doses give a He concentration fairly constant ($\sim 2.0 \times 10^{21}$ at cm^{-3}) through the damaged area which is expected to have a thickness stretching from 0.16 to 1.20 μm.

2.2. Small-angle X-ray scattering

SAXS experiments were performed on the French CRG-D2AM beamline at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The energy of the incident beam was fixed at 9.6 keV and the data acquisition was carried out using a charge-coupled device (CCD) camera. More details on the beamline can be found in Ref. [22]. In order to perform *in situ* measurements, a furnace designed in the SIMAP laboratory and consisting of a heating resistor wire regulated by thermocouples positioned in the vicinity of the sample was used. Cooling was achieved using a liquid circulation system at about 283 K. To avoid any contamination of the sample by direct contact with the metal of the furnace, its clamping was done with carbon foils.

The SAXS set-up (size of the beam stop, sample-to-detector distance) was chosen to characterise nanocavities with sizes ranging from 1 to 10 nm. This corresponds to an accessible q range varying from 0.02 up to 0.25 $Å^{-1}$, where q is the amplitude of the scattering vector. The data were acquired in transmission mode [23], which requires mechanical polishing of the samples so that their final thicknesses reach < 100 μm. The exact thickness e_{tot} (64 μm for (1 0 0) Si and 75 μm for (1 1 1) Si) was determined by measuring the X-ray absorption of each sample.