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Defects in Ge caused by sub-amorphizing self-implantation: Formation and dissolution

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ABSTRACT

High Resolution X-Ray Diffraction (HRXRD) was used to study the strain evolution of lattice defects formed in an array of B delta layers grown by Molecular Beam Epitaxy (MBE) and damaged by sub-amorphizing Ge self-implantation. The MBE structure was implanted at room temperature (RT) with 840 keV Ge at a dose of 1.5×10^{12} Ge/cm^2. First of all, we observed a RT strain reduction of ~40% with respect to the strain value found in the just-implanted sample. This strain ageing phenomenon saturates in about 5 months. Then, the complete defects dissolution was monitored by *in-situ* HRXRD during isochronal annealings. Three others strain-recovery steps were identified, the last at $T=157$ °C. Moreover, Secondary Ion Mass Spectrometry performed after the strain recovery did not detect any B diffusion till T was raised up to 840 °C, measuring in this case a B diffusion equal to the equilibrium one. The whole set of data will be discussed and compared with existing literature.

1. Introduction

With the continuing miniaturization of state-of-the-art metal oxide semiconductor (MOS) devices, conventional scaling methods are becoming less and less effective. Similarly, the effects of global or local strain to enhance channel mobilities are not considered sufficient for future technology nodes. As a consequence, the integration of alternative materials is taken into consideration. Germanium, with its significantly higher carrier mobilities with respect to silicon, is today one of the primary candidates especially for pMOS transistors [1,2]. A main obstacle against a break-through of this technology is that the research on bulk germanium and its properties was nearly abandoned more than twenty years ago both for technological and for economic reasons. So, despite the renewed interest in this material, relatively little knowledge of the defects caused by ion-implantation in Ge exists. In particular, if in the very last years some studies about Ge amorphization and the related End Of Range (EOR) defects started to appear [3–5], the information on defects formation and evolution under sub-amorphizing ion implantation is almost absent. To the knowledge of the authors, only Hickey and coworkers performed an investigation, based on Transmission Electron Microscopy (TEM) measurements, of defects formation and dissolution in bulk Ge which underwent sub-amorphizing implantations [6].

Hence, the purpose of the study reported in this paper is to investigate carefully the defects formed in Ge as a consequence of sub-amorphizing self-implantation. We modified the experimental strategy of Ref. [6] by using High Resolution X-Ray Diffraction (HRXRD) instead of TEM and using an array of boron delta layers grown in the Ge lattice by Molecular Beam Epitaxy (MBE). The choice of HRXRD as the main investigation tool relies on its higher sensitivity to very small point defects detection with respect to TEM [5,7,8]. Moreover, HRXRD does not require any sample preparation, avoiding possible artifacts of TEM analyses [6]. Finally, the use of an array of MBE B delta layers enabled us to obtain, by Secondary Ion Mass Spectrometry (SIMS), additional information on the interaction between the Ge self-interstitials (Is) generated by the implantation and B. In fact this dopant was chosen since it was recently demonstrated both theoretically [9] and experimentally [10] that its diffusion in Ge occurs via Is mediation.

2. Experimental procedure

A <001> Ge sample containing five B-delta doped layers at a concentration level of 4×10^{18} B/cm^3 and placed at 100, 300, 500, 700 and 1000 nm under the surface was grown by MBE. Then the sample underwent Room Temperature (RT) self-implantation with 840 keV Ge at a fluence of 1.5×10^{12} Ge/cm^2.

HRXRD Rocking Curves (RCs) ($\omega-2\theta$ scans) were recorded around the (004) reciprocal lattice point using a Philips X'Pert PRO MRD diffractometer equipped with a Bartels Ge (220) four-crystal

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monochromator and a parabolic mirror, using a channel-cut Ge (220) analyzer before the detector (triple-axis configuration with an angular acceptance of 12 arcsec). The Cu $K_{\alpha 1}$ radiation (~8 keV) was selected as the probe. The tube settings were 40 kV and 40 mA, respectively. The presence of a parabolic mirror and of an Anton Paar DHS 900 hot stage allowed the collection of *in-situ* (during annealing in N_2 atmosphere) and fast (360 s) diffraction measurements during a linear annealing ramp (the temperature was increased by 3 °C every 11 min from RT up to 330 °C) (for more details see ref. [7]). Perpendicular strain ($\varepsilon_\perp$) profiles were extracted by simulating RCs with a code exploiting the dynamical diffraction theory [11].

B chemical profiling was obtained by SIMS analyses with a Cameca IMS-4*f* instrument, using a 3 keV O_2^+ analyzing beam.

Ex-situ annealings at T = 840 °C for 135 min were performed in a conventional furnace in vacuum (10^{-5} mbar). In order to avoid any degradation of the Ge surface, the annealings were obtained with proximity capping of Ge, i.e. covering the sample surface with a piece of virgin high purity Ge.

3. Results and discussion

In Fig. 1 the RCs of a 5 mm × 5 mm slice of the investigated sample both before and just after the implantation process (as-implanted (AI) sample) are shown (closed and open circles, respectively). In addition, the RC made five months later on the same AI sample kept at RT is also reported (open diamonds). From a qualitative point of view, the appearance of a pronounced shoulder at negative angles just after the implantation is indicative of positive perpendicular lattice strain, i.e. of interstitial-type defects [5]. Moreover, the reduction of this shoulder, connected with the presence of positive lattice strain and well visible in the RC related to the same sample kept at RT for five months (see the arrow in Fig. 1), clearly indicates the metastable nature of part of the defects created by the self-implantation.

Quantitative information can be extracted by the simulations (continuous lines of Fig. 1) of the RCs related to the implanted sample, obtaining the corresponding $\varepsilon_\perp$ profiles reported in Fig. 2.

It is clear that after five months the $\varepsilon_\perp$ profile, even if retaining its shape, considerably lowers its value. More in detail, it is possible to calculate the strain integral ($I_{Strain} = \int_{0nm}^{700nm} \varepsilon_\perp dx$) associated to each profile, finding an I_{Strain} lowering of ~40%. This result was not affected by a possible non homogeneity of the irradiation fluence. In fact, as mentioned above, the HRXRD measurements were made on the same small slice of the AI sample.

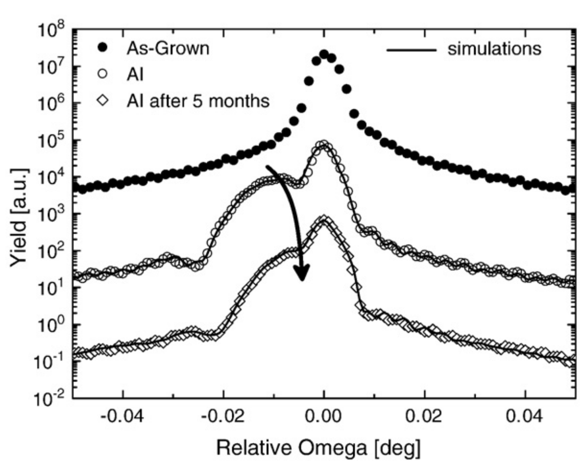

Fig. 1. (004) RCs of the as-grown sample before and after Ge implantation (closed and open circles, respectively). RC of the AI sample after five months RT annealing (open diamonds). The continuous lines represent the simulations. The arrow indicates the post-implantation ageing. Experimental data are offset for clarity.

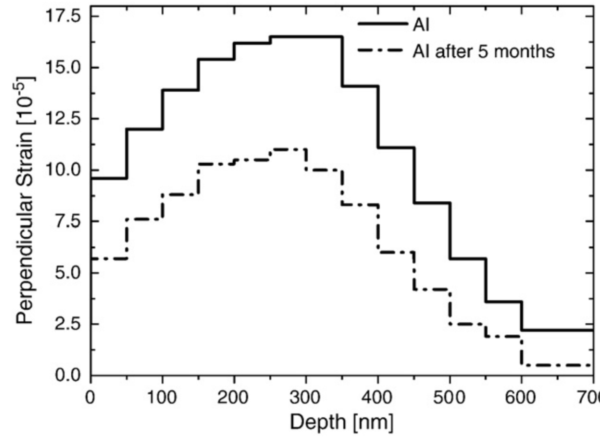

Fig. 2. Perpendicular strain profiles of the AI sample just after implantation and after ageing (continuous and dash-dotted lines, respectively).

This is the first experimental observation of lattice strain ageing in self-damaged germanium. More in general, this phenomenon was detected for P-implanted silicon [12], but it was never observed in the case of self-implanted Si.

Under the hypotheses that (i) this strain (i.e. damage) ageing is related to the dissolution of a particular type of defect created by the implantation process, that (ii) the strain amount is proportional to the abundance of this particular defect and that (iii) its dissolution occurs exponentially with a constant decay time τ, this last quantity can be expressed by the following equation:

$$\tau = \frac{1}{\nu_0} e^{\frac{E}{k_B T}}. \tag{1}$$

In Eq. (1) ν_0 is the attempt frequency of the process, T is the temperature, k_B is the Boltzmann constant and E represents the activation energy of the process. Considering ν_0 equal to the Ge phonon frequency ($\approx$10 THz), i.e. supposing that the strain ageing is a process simply thermally activated and not mediated by interaction with other species, we can obtain an estimation for E: $\approx$1.2 eV. This value is in agreement with the theoretical estimations of the Is migration energy ((1.0–1.4) eV) [13]. As a consequence, according to this picture, the strain ageing is connected with the dissolution of single Is created by the self-implantation process.

After the complete exhaustion of the strain ageing, which was found to occur in 5 months, in order to promote the complete strain (i.e. defects) dissolution we collected, as described before, *in-situ* isochronal RCs during thermal annealing of the sample.

In Fig. 3 the I_{Strain} as a function of the annealing temperature is reported (open circles). The pristine I_{Strain} value of the AI sample is evidenced (star), together with the I_{Strain} lowering due to the ageing. It is clear that the I_{Strain} is not a monotonic function of T and that the I_{Strain} recovery occurs in the (74–173) °C thermal region.

In principle, defects dissolution may occur in many steps, each of which has to overcome a particular energy barrier to take place. In order to evidence this possibility, the derivative of the I_{Strain} with respect to T (a sort of "I_{Strain} evolution speed" plot) was performed and shown in Fig. 4. In addition to the first dissolution process occurring at RT and that will have its maximum velocity for T < 74 °C, i.e. the temperature at which the I_{Strain} starts again to dissolve (see the arrows n° 1 of Fig. 4), this plot shows the presence of three other main processes of defect dissolution. The maximum speed of these processes, indicated in Fig. 4 by the arrows n° 2, n° 3 and n° 4, are thermally located at $T_2 = 93$ °C, $T_3 = 118$ °C and $T_4 = 157$ °C, respectively. The simplest interpretation of Fig. 4 is that self-implantation damage gives rise to four different types