Materials Science in Semiconductor Processing 42 (2016) 196–199

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

# Oxygen behavior in germanium during melting laser thermal annealing

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ARTICLE INFO

*Article history:*
Received 10 June 2015
Received in revised form
22 July 2015
Accepted 22 July 2015
Available online 30 July 2015

*Keywords:*
Germanium
Laser annealing

ABSTRACT

The diffusion of oxygen and its interactions with dopants during laser thermal annealing (LTA) in the melting regime is investigated. O is shown to penetrate from the surface and to diffuse during LTA both into germanium un- and also implanted with arsenic or boron. In the latter cases, the diffusion is unaffected by As, whereas it is significantly reduced by B. Accordingly, the electrical activation of As and B are respectively un-and anti-correlated with O. Therefore, it is concluded that O does not interact with As nor in the melt, nor in the solid phase during the cooling transient. On the other hand, the B–O clustering reported in literature to explain the B deactivation during LTA [Impellizzeri et al., J. Appl. Phys. 113(2013) 113505] occurs already in the liquid phase during the regrowth. Thence, the present data provide noteworthy results for the LTA implementation in future complementary metal-oxide devices.



## 1. Introduction

Germanium is the main candidate for replacing silicon as substrate for future complementary metal-oxide transistors due to its higher mobility of charge carriers that makes it able to attain higher drive current [1,2]. However, several issues need to be solved concerning the diffusion and activation of dopants, especially in the case of *n*-type ultra-shallow junctions (USJ) either due to the low solid solubility of the group-V elements, to their quick diffusion at high concentrations owed to the pairing with doubly negatively charged vacancies, and also due to their interaction with extended defects [3–7]. In order to overcome the above issues, laser thermal annealing (LTA) in the melting regime is studied as an advanced annealing technique, being able on one hand to activate dopants in concentrations far exceeding the equilibrium solid solubility, and also to control the diffusion by tuning the irradiation (or exposure) conditions [8–10].

However, recent studies performed by our group about LTA subsequent to ion-implantation into Ge evidenced the negative role of oxygen contaminants on *p*-type doping with boron, in particular by promoting the precipitation of small inactive B–O clusters with a mechanism which is not yet well understood [11,12]. These studies also evidenced that the O penetration and its detrimental effects on B activation are reduced if the native Ge oxide is removed by dipping the samples in hot de-ionized water before the laser exposure, but the reduction effects are eventually not complete. Concerning the activation of *n*-type dopants by LTA, the role of contaminants was not explored yet. Indeed, we recently tested the laser irradiation on Ge implanted with arsenic succeeding in a new record for the donor concentration in the Ge:As system, but the dopant was unexpectedly only partially activated [13].

Here we present a systematic investigation on the O behavior into Ge doped with As or B in comparison with un-doped samples irradiated with similar laser conditions, with the aim of describing the O diffusion and O-dopant interaction dynamics in such annealing regime as well as clarifying their influence on the electrical activation of As and B during LTA.

## 2. Experimental

(100)-oriented Czochralski-Ge wafers were implanted with $As^+$ ions at 40 keV $3 \times 10^{15}$ As/cm$^2$ and $B^+$ ions at 20 keV $1 \times 10^{15}$ B/cm$^2$. In both of the case, no superficial oxide capping has been used. Then, the samples were rinsed in de-ionized water at 50 °C for 1 min before preforming the laser processing, in order to remove most of the superficial oxide layer [14]. Afterwards, LTA with $\lambda = 308$ nm and 28 ns pulse duration was performed in

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http://dx.doi.org/10.1016/j.mssp.2015.07.066
1369-8001/

vacuum by using a Lambda Physik LPX 205 XeCl excimer laser equipped with a beam homogenizer forming $5 \times 5$ mm$^2$ spots. The investigated energy densities were 530, 630 and 650 mJ/cm$^2$, corresponding to different maximum melt depths (MMDs). Only for the highest energies, single- and multi-pulses regimes (3 or 10 shots) were tested. As a reference, also un-implanted Ge was subjected to rinse in hot de-ionized water and irradiation with 1 and 10 pulses.

Chemical As, B and O depth profiles were measured by Secondary Ion Mass Spectrometry (SIMS) using a Cameca IMS-4f instrument probing with a $Cs^+$ primary beam and analyzing secondary $CsAs^+$, $CsB^+$ and $O^-$ ions respectively. All the concentrations of each specie as well as the depth scales were calibrated by using commercial certified standards, with accuracy of 10% and by measuring the crater depths with a profilometer and assuming constant sputtering rates, with an overall accuracy of 2%.

Finally, the carrier concentration profiles were obtained by Spreading Resistance Profiling (SRP) measurements using a SSM 150 system with probe loading weight of 5 g [15,16]. The conversion of resistance data into resistivity was done by means of homogeneously doped Ge samples of known resistivity. Then, the resistivity profiles were converted into carrier concentration ones by using resistivity versus impurity concentration curves reported in literature [17].

## 3. Results and discussion

Fig. 1a reports the chemical concentration profile of arsenic and boron as measured by SIMS after 10 laser shots (symbols) at energy densities of 650 mJ/cm$^2$ for As (triangles) and of 630 mJ/cm$^2$ for B (circles) respectively. Profiles before LTA are also shown as a reference (dashed lines). Significant diffusion of the dopants after the laser processes can be noticed up to the MMD which, for the energy densities considered, correspond to depths of about 120–130 nm. This is a result of the confinement of the diffusion processes within the liquid phase that is characterized by larger diffusivity with respect to the solid substrate [18,19].

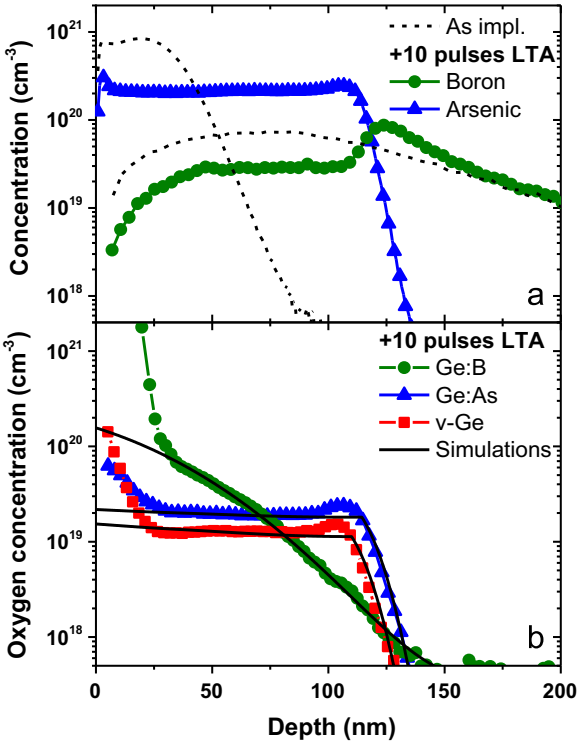


**Fig. 1.** (a) B (circles) and As (triangles) concentration profiles as measured by SIMS after ion implantation (20 keV $1 \times 10^{15}$ B/cm$^2$ or 40 keV $2 \times 10^{14}$ As/cm$^2$ respectively) and 10 pulses LTA (at 630 mJ/cm$^2$ for B and at 650 mJ/cm$^2$ for As). As implanted profiles before LTA are also shown (dashed lines). (b) O concentration profiles measured in the same samples of panel (a), and in an un-implanted Ge sample after 10 pulses LTA at 650 mJ/cm$^2$. Best fits of O diffusion profiles are also reported (continuous lines).

Fig. 1b shows the oxygen concentration as function of the depth measured by SIMS in the same samples of Fig. 1a, i.e. after ion implantation of As (triangles) or B (circles) and subsequent LTA. The profiles obtained in the un-implanted samples (squares) after similar laser processing is also shown for comparison. The surface peaks, extending down to a depth of about 20 nm are an artifact of the SIMS technique, related to the presence of a superficial native oxide and due to atomic relocation during the analysis. However, an O penetration is clearly observed in all the samples as a result of LTA, despite the dipping in hot de-ionized water prior to the laser exposure. This is in agreement with what is observed in Ref. [11] and it is due to O diffusion from the native oxide, which is perhaps only incompletely removed by the dip and/or partially regrown before the LTA. It can be noticed that the O after 10 pulses almost completely redistributes within the MMD both in the un- and in As-implanted sample, resulting in similar depth profiles. Quite surprisingly, O diffusion is instead significantly reduced by the presence of B being the profile barely reaching the MMD. Qualitatively similar conclusions as above are obtained from the samples processed by single pulse and at lower energy density (not shown).

In order to get more insights on the O diffusion, the SIMS profiles are fitted with a simple simulation code written in ANSI-C and developed by our group, which numerically solves the Fick's equation, implementing the boundary conditions at the surface and at the MMD. In particular, the MMD was modeled as a 'perfect mirror' and the surface as a source with a fixed concentration $C_0$ that was left as a free parameter in the fitting procedure. O diffusion coefficient $D$ was assumed to be constant with depth and time and the best fits are obtained by leaving the product $Dt$ as a free parameter, where $t$ is the total diffusion time (i.e. the total duration of the molten phase). Best fits, reported in Fig. 1b (solid lines), satisfactorily describe the experimental O profiles obtained after 10 pulses at 630–650 mJ/cm$^2$. Fits of similar qualities have been obtained for single and 3 pulses and at a lower energy density (not shown).

Fig. 2 reports $Dt$ values extracted by the simulations as a function of the number of pulses relative to samples after LTA at 630–650 mJ/cm$^2$ in un- (squares) and in As- (triangles) or B-implanted germanium samples (circles). It is clear that data relative

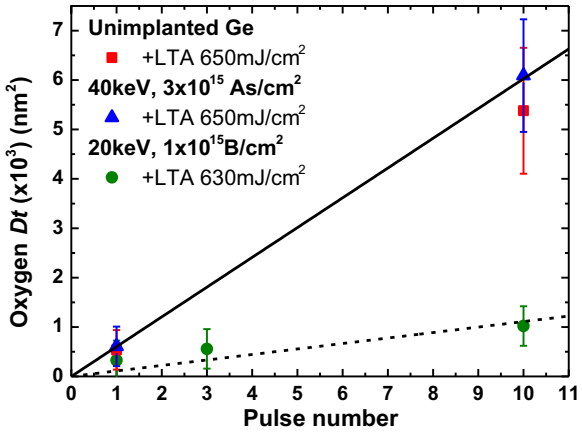


**Fig. 2.** $Dt$ as determined by the fits of the O concentration profiles versus the number LTA pulses. The linear fit for samples un- and implanted with As (solid line) or with B (dashed line) are also reported.