



Indiffusion of oxygen in germanium induced by pulsed laser melting

R. Milazzo^{a,*}, M. Linser^a, D. Scarpa^b, A. Carnera^a, A. Andrighetto^b, E. Napolitani^a

^a Dipartimento di Fisica e Astronomia, Università di Padova and CNR-IMM, Via Marzolo 8, 35131 Padova, Italy

^b INFN Laboratori Nazionali di Legnaro, Italy



ARTICLE INFO

Keywords:

Germanium
Oxygen
Contamination, laser annealing

ABSTRACT

A systematic study of the indiffusion of oxygen in germanium induced by pulsed laser melting (PLM) is reported. In order to evidence the impact of the experimental parameters, different processing conditions have been compared, i.e. with or without pre-PLM etching of the Ge native oxide by H₂O or HF dip, Air or N₂-rich atmosphere, and single or multi-pulse PLM. Oxygen indiffusion is always observed with surface concentration above $1 \times 10^{19} \text{ cm}^{-3}$ for all the processing conditions. Pre-PLM surface chemical treatments seem to have no significant influence in terms of the oxygen penetration, although HF allows lower surface roughening. On the contrary, a processing atmosphere with reduced oxygen concentration is more efficient in reducing the overall O indiffusion. The present experimental results are crucial in view of the implementation of the PLM technique for highly doped Ge as well as to design studies where contamination issue might be crucial.

1. Introduction

Germanium attracted a renewed interest for its high performances in a large number of actual hot topics such as micro- and optoelectronics [1–5] as well as high purity Ge gamma-ray detectors [6]. In particular, since the successful introduction of high-k materials [7] it became the foremost candidate for replacing silicon as substrate in sub-15 nm electronic devices [8]. The main advantages are essentially due to its higher carrier mobility (the highest for holes among semiconductors), as well as interesting optical properties, together with the ease of integration with the actual Si-based technology [1].

Nevertheless, implementation of Ge in the above devices requires in most cases very high doping levels ($> 10^{20} \text{ atom/cm}^3$) [8], i.e. above the solubility for most of dopants [9], together with shallow or even ultra-shallow doping profiles [8]. Fulfilling these requirements is challenging for every dopant, but it is particularly difficult for n-types, where extrinsic doping results into diffusion enhancement [10,11]. For this reason, pulsed laser melting (PLM) is a very promising technique [8], being able to promote ultra-fast liquid phase epitaxial regrowth in a shallow layer [12]. As a consequence of the very non-equilibrium nature of the process, dopants can be activated well above the equilibrium solid solubility [13]. At the same time, diffusion is confined within the molten layer, whose thickness can be easily tuned by varying the laser energy density [12].

Recently, studies on excimer PLM following ion implantation of As, P or B revealed a pronounced oxygen contamination (up to 10^{20} atom/

cm^3) [14,15]. In the case of B, oxygen is detrimental for the electrical activation [16,17], and an improvement both in terms of the oxygen amount as well as B activation is observed by performing PLM after an etching of the superficial native oxide with H₂O. However, this procedure is known to remove only the GeO₂ that is soluble in water [18], so leaving open the question whether a more aggressive etching would solve the problem. Despite the above observations, only few and scattered information have been reported so far on how the PLM process could be optimized in order to reduce such O contamination. In this paper we investigate possible methods to reduce the O contamination in Ge after PLM, by focusing on O penetration and comparing different pre-PLM surface treatments as well as annealing atmospheres.

2. Materials and methods

(100)-oriented Cz-Ge ($\rho > 40 \Omega \text{ cm}$) was cut into different pieces that undergone two different types of chemical processing: a single dip in distilled H₂O at 50 °C for 5 min, to remove only the water soluble GeO₂ [19], or a treatment based on HF cycles, in order to fully remove both the native GeO₂ and GeO, so leaving a relatively stable Ge-H terminated surface [20]. The latter method consists of a preliminary dip in distilled H₂O at 50 °C for 1 min (removing most of the native GeO₂), 5 consecutive dips in HF (10%, electronic grade) for 2 min each followed by 1 min in distilled H₂O at room temperature and, as a final step, a quenching dip in ethanol. After surface preparation, the samples were conserved under vacuum ($\sim 10^{-2} \text{ mbar}$), until few minutes before the

* Corresponding author.

E-mail address: ruggero.milazzo@unipd.it (R. Milazzo).

laser processing, when they have necessarily been exposed to air. In parallel, a set of the original virgin Ge samples were preserved as reference.

Afterwards, Nd:YAG PLM with third harmonic generator ($\lambda = 355$ nm and 7 ns pulse duration) was performed by using a Quantel YG980 forming a circular spot of 7 mm diameter with nearly flat energy density in the inner 3 mm. The samples were processed with an energy density of 400 ± 20 mJ/cm², (where the error of ± 20 mJ/cm² takes into account for both the reproducibility and the uniformity in the above 3 mm inner region, where all the measurements reported in the following have been made) corresponding to a maximum melt depth (MMD) of about 150 ± 20 nm. Both single- and multi-pulses regimes (5 or 20 shots) were tested on treated- and on untreated-sample, either in ambient or in N₂ enriched atmosphere obtained by blowing a constant flux of pure N₂ gas towards the sample surface during laser treatments.

Chemical O depth profiles were measured by Secondary Ion Mass Spectrometry (SIMS) using a Cameca IMS-4f instrument with a 7.25 keV Cs⁺ primary ion beam and analyzing secondary O⁻ ions. The sputtering raster size was 175×175 μm^2 while the signal was collected by an inner circular area of 60 μm diameter. O concentrations were calibrated against commercial certified standards with accuracy of $\pm 10\%$ and depth scales were calibrated by measuring the crater depths with a profilometer and assuming constant sputtering rates, with an overall accuracy of $\pm 2\%$.

In order to assess if the investigated pre-PLM surface treatments and the processing atmosphere have any impact on the surface morphology during PLM, atomic force microscopy (AFM) analyses have been performed with a Veeco CP II instrument operating in tapping mode. At least three 5×5 μm^2 images for each sample were acquired from different regions within the inner part of the laser spot and analyzed with Gwyddion [21]. Small errors in the scans, such as misaligned rows, as well as artefacts, which can be caused by the tubular piezoelectric motion, were respectively corrected via software or removed subtracting a polynomial background. Finally, the root mean square (RMS) of the roughness was extracted.

3. Results

Fig. 1 reports the oxygen concentration as function of the depth

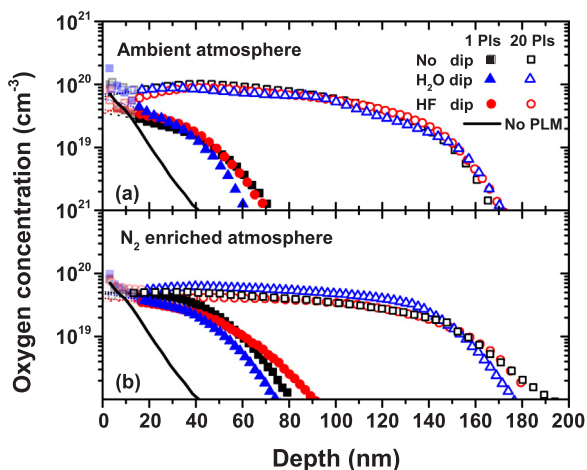


Fig. 1. Oxygen concentration profiles in Ge as measured by SIMS before (solid line) and after single- (solid symbols) or multi-pulse (open symbols) PLM at 400 ± 20 mJ/cm² (squares) both performed in ambient (a) and in N₂ enriched atmosphere (b). Data are also distinguished according to different pre-PLM surface treatment: no dip (squares), H₂O at 50 °C for 5 min (triangles) and $5 \times$ HF dip for 2 min (circles). Extrapolations in the first 15 nm from the surface are also reported (dash lines), where the technique exhibits significant artifacts (shaded symbols).

after 1 shot (closed symbols) or 20 shots (open symbols) of PLM at 400 ± 20 mJ/cm² as characterized by SIMS. The profiles are split according both to the different atmosphere used during the laser irradiation, i.e. ambient (above) or N₂-enriched atmosphere (below), as well as to pre-PLM surface treatments: no treatment (squares), H₂O dip (triangles) or HF dip (circles). The signal recorded in the un-irradiated sample (solid line) is also included, where oxygen is detected as a result of the atomic relocation of the native oxide during the analyses. Hence, it is representative of the resolution and so it can be used as reference in order to evaluate the oxygen penetration as a result of laser irradiation. The profiles in Fig. 1 also exhibit a peak in the first ~ 15 nm close to the surface (shaded points). This effect is attributed to typical artifacts of the SIMS technique, due to the sputtering-induced relocation of the O atoms contained in the residual native oxide. In order to reduce the above artifacts, extrapolations from deeper regions have been performed (dashed lines).

The profiles are systematically deeper after 1 pulse for any experimental condition, so evidencing the oxygen contamination induced by PLM processing. The effect of the MMD is particularly evident after 20 shots, as the O penetration depth increases up to reaching 150 ± 20 nm, where a sharp concentration decrease is clearly visible. This is a well-known effect in PLM processing, due to the drop of the diffusion coefficient by several orders of magnitude in the solid phase with respect to the liquid one [22,23]. The resulting value of MMD is in good agreement with simulations based on heat diffusion equation (Laser Induced Melting Predictions – LIMP, Harvard simulation software package [24]). Fig. 1 does not evidence significant differences between the different surface pre-PLM treatments. The little deviations on the penetration depth (of the order of 20 nm) are very likely caused by fluctuations of the laser energy density within ± 10 mJ/cm², as determined by measurements of the laser power performed in continuous regime. On the contrary, lower O contaminations seem to be present after multipulse PLM processes performed under N₂-rich atmosphere.

In order to quantitatively compare the different processing conditions, the overall O areal densities have been calculated from the SIMS profiles, as reported in Fig. 2. In particular, the figure reports the areal densities as function of the pulse number after laser irradiation in

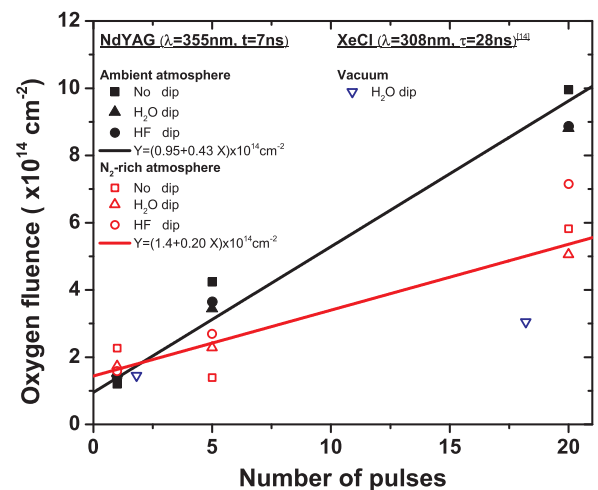


Fig. 2. Oxygen fluence after PLM using a NdYAG laser at 400 ± 20 mJ/cm² in ambient (closed symbols) and inert atmosphere (open symbols) is plotted versus number of pulses. Different pre-PLM surface treatments are distinguished: no dip (squares), H₂O at 50 °C for 5 min (triangles) and $5 \times$ HF dip for 2 min (circles). Literature data recorded after PLM by means of a XeCl laser at 650 mJ/cm² in vacuum are also reported as a reference (open reversed triangles). In the latter case, the number of pulses have been multiplied by a factor of 1.8 in order to take account for higher diffusion effects induced by the longer pulse duration for the Xe-Cl [14].

Download English Version:

<https://daneshyari.com/en/article/7117320>

Download Persian Version:

<https://daneshyari.com/article/7117320>

[Daneshyari.com](https://daneshyari.com)