1. Introduction

In the last two decades, germanium (Ge) has become one of the most studied semiconductors and now it is applied in many research and applicative fields such as microelectronics, photonics, solar energy and radiation detectors. In order to improve performances, a great effort has been demanded to find new doping technologies with the main aim of the formation of shallow and highly doped junctions for nano- and micro-electronic applications [1]. As a consequence, a deep knowledge about intrinsic defects (vacancies and interstitials) and their influence on diffusion and activation of impurities during doping processes was recently gained in germanium (see e.g. [2, 3] and reviews [4, 5]).

Typical doping processes for many Ge applications involve thermal diffusion by a dopant source or ion implantation followed by thermal annealing of the damage. More recently, interesting studies have also investigated laser thermal...
detectors are available with a segmented p junction, with high energy resolution [11, 12]. Currently, n-type gamma contact in HPGe to improve the performance of gamma trackers of suitable doping processes to form a segmentable n-type con-

struc-ure, which is the high purity of the intrinsic part with less than 10^{10} \text{cm}^{-3} doping atoms. As a matter of fact, doping pro-
ces-ses to make junctions promote the diffusion of impurities and defect states throughout the material and the incorpora-
tion of external contaminants through physical processes that are thermally activated. All these species such as dislocations, vacancy complexes, shallow impurities (Cu, Ga, B, Li, etc) and deep-level contaminants (Cu, Fe, Zn, etc) can increase the doping level of HPGe and also act as generation/recombination centers for free charge carriers, thus affecting the operation of any device [14]. Among the aforementioned, copper is one of the fastest diffusants in Ge at low temperature [15].

In order to allow good performances of a gamma detector, the surface doping process must preserve the 10^{10} \text{cm}^{-3} doping limit in the bulk. Such a low level is much more demanding than what is typically requested for other common applications (microelectronic, optoelectronic, photovoltaic devices), where a background doping level between 10^{14} and 10^{18} \text{cm}^{-3} is generally present [16]. On the other hand, in the case of high purity silicon, used e.g. in silicon drift detectors, a contaminant threshold limit of 10^{15} \text{cm}^{-3} is requested to guarantee the optimal performance of the device [17]. The 10^{10} \text{cm}^{-3} limit makes quite difficult a direct measure of the contaminants (e.g. SIMS detection limit in Ge is above 10^{14} \text{cm}^{-3} for most of the contaminants [18]) and electrical measurements are one of the few possibilities.

Keeping this in mind, possible candidates for HPGe doping have to be selected maintaining the thermal budget as low as possible and using high purity dopant precursors.

In particular, our group investigated P and Ga diffusion from SOD sources [19]. Sb equilibrium diffusion from a sputtered source [20] and LTA diffusion of sputtered Sb [12]. Among possible diffusion doping processes, with the exception of lithium that has a too high diffusivity, P and Ga are the faster n-type and p-type diffusant elements, respectively, that could in principle allow reducing the thermal budget for the process [4]. Sb sputtering source is available at a very high purity with potential benefits for HPGe applications even if Sb is a slower diffusant than P.

In this paper, four-wire electrical measurements versus temperature were performed on HPGe samples treated with the aforementioned processes. Data about the concentration, type and mobility of charge carriers generated by thermally-activated bulk impurities were collected and modelled, in order to find a possible process window for doping HPGe without contaminating the bulk material.

2. Experimental

2.1. Sample preparation

Two (100) HPGe wafers of p- and n-type, 2 mm thick, with impurity concentration in the range (0.4 to 2) \times 10^{15} \text{cm}^{-3} and a dislocation density of about 2000 counts cm^{-2}, were supplied by Umicore. They were manually polished in order to smooth surfaces and then cut into 10 \times 10 \text{mm}^2 samples using an automatic dicing machine (Disco Corporation, Tokyo, Japan). Each sample was cleaned with hot 2-propanol, hot deionized water and HF 10% wt. to remove dicing adhesive residue and native oxides. After, a more aggressive etching bath was done in HNO_3(65%):HF(40%) 3:1 solution for 5 min, in order to remove about 100 \text{µm} and consequently the residual mechanical damage from surfaces [21].

Two samples of p and n-type were characterized as reference samples (sample codes Rp and Rn, respectively, in table 1), in order to verify the concentration of active impurities specified by the supplier.

Further HPGe slices, prepared in the same way, were sub-
sequently doped at the surface with different approaches. One sample was doped by B ion implantation, a standard technique used for the formation of the p-type contact in HPGe detectors (sample code B in table 1). The following parameters were used for the implantation: 22.6 keV ion energy and 1 \times 10^{15} \text{cm}^{-2} dose.

Samples from P1 to LTA in table 1 were prepared according to innovative doping methods that our group recently...
tested and optimized with the specific aim of HPGe doping [12, 19, 20]. Here we report a brief description of all processes, summarizing the main features of each one, while the full technical description is reported in detail in specific cited references. The selected process parameters used in this work are in general those with the as low as possible thermal budget to obtain a good junction.

In detail, samples P1, P2 and Ga were doped by P and Ga spin-on doping (SOD), using the experimental technique described in [19]. Commercial sources (sol-gel precursors, Filmtronics, Butler PA, USA) containing P and Ga were homogeneously deposited above the sample front surface by spin-coating. Then, the films underwent a curing stage at 130 °C for 30 min, in a N₂ atmosphere at 10% relative humidity. Finally, each sample was capped with Si and quartz humidity. Finally, each sample was capped with Si and quartz.

One sample (Sb code) underwent an equilibrium diffusion process starting from an Sb precursor. In this case, a thin film of pure Sb was sputtered on an auxiliary Si substrate (ACI Alloys Sb sputtering target, 99.999% purity with Cu content ≤0.01 mg kg⁻¹) and was placed in a quartz boat over the HPGe front surface at a distance of 8.5 mm. During the annealing performed at 605 °C for 30 min, Sb was released from the source and diffused inside HPGe without causing surface damages [20].

Finally, we also made a test (LTA sample code) by exploiting melting laser annealing as described in [12]. An ultra-thin film of pure Sb is sputtered directly on the HPGe surface through the aid of a mask, in order to form four square Sb sources of 1.5 mm side, at the vertexes of the square surface. Then, these four Sb sources were irradiated with a fast laser pulse of 7 ns. The laser pulse melts the first 150 nm of HPGe thus inducing Sb diffusion in liquid. The melt depth has been determined through SIMS measurements [12].

Table 1. List of all characterized samples, their codes and preparation details. The last three columns report the main bulk impurity data: the density of ionized bulk impurities (N), the total density of thermally-induced acceptor defects (Nt) and the final type of conductivity determined by Hall effect.

| Sample code | Starting conductivity | Annealing treatment | Surface treatment | Surface etching | N \( (\text{cm}^{-3}) \) | Nt \( (\text{cm}^{-3}) \) | Hall final conductivity |
|-------------|-----------------------|---------------------|------------------|----------------|-----------------|-----------------|----------------------|
| Ln          | n                     | —                   | —                | yes            | \( [8.7 \pm 1.5] \times 10^9 \) | —               | n                    |
| Rp          | p                     | —                   | —                | no             | \( [8.9 \pm 3.3] \times 10^9 \) | —               | p                    |
| B           | p                     | —                   | B impl.          | yes            | \( [9.5 \pm 2.1] \times 10^9 \) | —               | —                    |
| P1          | p                     | 611 °C 156 s        | P diff.          | yes            | \( [3.4 \pm 0.6] \times 10^{10} \) | [2.5 \pm 0.9] \times 10^{10} | —                    |
| P2          | n                     | 608 °C 621 s        | P diff.          | yes            | \( [2.0 \pm 1.0] \times 10^{11} \) | [2.1 \pm 1.0] \times 10^{11} | —                    |
| Ga          | p                     | 810 °C 766 s        | Ga diff.         | yes            | \( [1.1 \pm 0.1] \times 10^{14} \) | [1.1 \pm 0.1] \times 10^{14} | —                    |
| Sb          | n                     | 605 °C 1801 s       | Sb diff.         | yes            | \( [3.0 \pm 0.9] \times 10^{12} \) | [3.0 \pm 0.9] \times 10^{12} | —                    |
| LTA         | n                     | LTA                 | SiO₂ sputt.      | no             | \( [1.1 \pm 0.2] \times 10^{10} \) | —               | n                    |
| CAP         | p                     | 614 °C 1801 s       | SiO₂ sputt.      | no             | \( [7.8 \pm 1.0] \times 10^{12} \) | [7.8 \pm 1.0] \times 10^{12} | —                    |
| T1          | n                     | 611 °C 150 s        | —                | no             | \( [1.1 \pm 0.2] \times 10^{11} \) | [1.2 \pm 0.2] \times 10^{11} | —                    |
| T2          | n                     | 611 °C 150 s        | —                | no             | \( [4.8 \pm 1.6] \times 10^{10} \) | [5.7 \pm 1.8] \times 10^{10} | —                    |
| T3          | n                     | 610 °C 631 s        | —                | no             | \( [5.0 \pm 0.8] \times 10^{11} \) | [5.1 \pm 0.8] \times 10^{11} | p                    |
| T4          | n                     | 618 °C 1800 s       | —                | yes            | \( [2.2 \pm 0.3] \times 10^{12} \) | [2.2 \pm 0.3] \times 10^{12} | p                    |
| T5          | p                     | 624 °C 1800 s       | —                | yes            | \( [5.7 \pm 1.1] \times 10^{12} \) | [5.7 \pm 1.1] \times 10^{12} | —                    |
| T6          | n                     | 800 °C 666 s        | —                | yes            | \( [6.9 \pm 2.2] \times 10^{13} \) | [6.9 \pm 2.2] \times 10^{13} | p                    |
| T7          | p                     | 609 °C 552 s        | —                | no             | \( [9.9 \pm 1.5] \times 10^{11} \) | [9.8 \pm 1.5] \times 10^{11} | p                    |
Ge thickness was about 10 μm, much more than the highly doped zone that is confined in the first 0.5 μm for all the treatments.

Then, Au/Cr square pads (1.5 mm side) acting as contacts were sputtered at the corners of all the samples. All electrical measurements were done by using thin Cu wires bonded to Au/Cr pads through malleable indium.

### 2.2. Low T electrical measurements

Four-wire electrical measurements at low temperature were performed, according to the Van der Pauw method. The experimental set-up is a variable temperature Hall-effect measurement system provided by MMR Technologies. It consists of a small vacuum chamber containing a Joule–Thomson micro- meter refrigeration circuit, in which high-pressure N2 (~124 bar) is injected and expanded, provided with a ceramic stage for thermal contact with the sample, a capillary tubes system for N2 transport and injection, a rotary pump and a turbomolecular pump to achieve a vacuum level of about 5 × 10⁻⁵ mbar inside the chamber and, finally, a remotely-manageable temperature controller. A resistor is also present for the heating. With this apparatus a wide range of temperatures from 77 to 700 K can be investigated.

The sample is bonded to a Kapton printed circuit for electrical measurements, which are carried out with the use of a Keithley 2600 sourcemeter, a switch matrix, a customized acquisition software and a permanent magnet (0.5 T) for the Hall effect.

### 3. Results and discussion

#### 3.1. Experimental data

Figure 1 reports the results of bulk sheet resistance measurements with decreasing temperature, performed according to the Van der Pauw method. The measurements were done with a current of 1 μA, value chosen after testing a wide range of currents looking for a plateau of sheet resistances [22]. Due to non-ideal size and position of the electrical contacts, a geometrical correction factor of 1% was applied to all measured data [23]. This value was estimated by simulating the currents in the real contact geometry through finite element simulations done with COMSOL Multiphysics software (MEMS Module), as described in detail in [24] and comparing them to the ideal case of point contacts at the corners. As regarding measurement errors, due to electrical signal reproducibility we estimate a 10% error for the measurements on n-type samples (Rn and LTA); in all other cases, the error is below 5%.

Looking at figure 1, starting from room temperature the experimental sheet resistance rapidly increases until a maximum value is reached, which is very different from sample to sample (from 10⁵ to 5 × 10⁶ Ω sq⁻¹). Then, by lowering the temperature further, for all the samples the sheet resistance reverses its trend and slowly decreases.

An interesting result comes out from Hall-effect measurements at low temperature, done on a set of selected samples (see table 1, last column). At low temperature, all samples that had received a high-temperature annealing process showed positive carrier sign, even if their bulk was n-type before any treatment. The only samples that showed n-type carriers were the reference n-type HPGe and the sample that received Sb doping by LTA. This result is important because it shows that during high-temperature annealing in a standard furnace, a strong activation of acceptor levels occurs inside bulk HPGe, while LTA technique seems not to involve this kind of problem.

In order to better understand the sheet resistance data, the expected theoretical trends of sheet resistance as a function of temperature were calculated for different doping levels. By assuming a p-type Ge sample, with a thickness $t$, the theoretical sheet resistance $R_{\text{sheet}}$ can be calculated by:

$$ R_{\text{sheet}} = 1 / \left( t \rho \mu_p \right) $$

where $\rho$ is the extrinsic hole density and $\mu_p$ is the hole mobility.

In a p-type semiconductor with $N_a$ acceptor density, $p$ can be expressed by:

$$ p = \left( N_a \right) / 2 + \left( \left( N_a^2 / 4 \right) + n_i^2 \right)^{1/2} $$

where

$$ n_i = \left( \left( N_a N_c \right) \right)^{1/2} \exp \left( -E_a / (2k_BT) \right) $$

$N_a$ being the extrinsic acceptor density, $N_c$ and $N_a$ the valence and conduction band effective density of states, respectively [16].

In order to calculate sheet resistance curves, the variation of carrier mobility with temperature for different carrier concentrations has to be considered in equation (1). This was extrapolated from the literature data, particularly from [25, 26] for p-type and from [27, 28] for n-type. The literature mobility curves were digitized and fitted by power law trends, then the power law coefficients were interpolated as a function of the doping concentration in order to have access to the mobility at any temperature and dopant concentration [24].
In figure 1 all the theoretical sheet resistance curves as a function of temperature are shown for different p-type doping concentration (continuous lines). As can be observed, functions have all the same shape, but they present a different height in the plot depending on the carrier density. Each function is characterized by two slopes. Starting from room temperature (300 K), the first trend is typical of the intrinsic regime where \( p = n \) and it exponentially increases by decreasing temperature according to equation (3).

At a certain temperature value, the density of charge carriers originated from acceptors ionization \( N_a \) exceeds that of thermally activated carriers \( n_i \) and a trend reversal occurs entering the saturation regime where \( p = N_a \). The transition temperature is different for each sample because the lower the impurity concentration, the lower the temperature at which \( N_a > n_i \) holds. In the saturation regime, the decrease of sheet resistance by decreasing temperature derives from carrier mobility increase due to less lattice vibrations.

The dashed line represents the sheet resistance trend for a \( 1 \times 10^{10} \) cm\(^{-3} \) n-type doped germanium and is calculated by the n-type version of equation (2). As can be noted, the low temperature sheet resistance drop shows a different slope depending on the impurity type (p- or n-) due to different mobility dependence on temperature [16].

### 3.2. Contaminant concentration analyses

Sheet resistance experimental data vary with temperature as expected, in fact the shape of experimental curves is the same as the one of theoretical lines. Interestingly, experimental curves lie on different heights in the plot, meaning that our samples are characterized by different bulk impurity concentrations.

Sheet resistance data can provide the carrier density by inverting equation (1). To do this, the literature mobility can be used as described before, or alternatively mobility estimates by Hall measurement could be used. In figure 2 a comparison between the literature and experimental values of mobility is reported for samples Rn, Rp, LTA, T3, T4, T6, T7, together with measuring temperatures. Data present a substantial agreement in a wide range of values; discrepancy can be attributed to low accuracy in our experimental measurements. As a matter of fact, since Hall measurements are much more sensitive to contact geometry, we estimated 15% correction due to square contacts, but larger variation may be due to poor definition of the contact shape geometry due to indium pads. Another possible explanation for the discrepancy of mobility with respect to the literature may be the fact that our samples may not be pure n- or pure p-doped material, but their carrier concentration could come out by a partial compensation of both doping types. If this were true, a lowering of mobilities with respect to the literature could be explained by the scattering occurring by both charged impurities. Due to the very low concentration of dopants involved, a deeper insight into this point is very difficult. For this reason and considering also the fact that we performed mobility measurements only in a subset of samples and temperatures, we decided to adopt the literature mobilities to calculate carrier densities, thus accepting the fact that they may be systematically underestimated by maximum 30% due to the uncertainty in mobility values.

The carrier density experimental curves, representing the density of electrically active charge carriers as a function of \( 1/k_BT \), are shown in figure 3. The intrinsic and saturation regimes are clearly distinguishable and the carrier density in the saturation regime corresponds to the density of ionized bulk impurities. Hence, for each curve we have taken the average concentration value \( N \) in the first 50 K of the saturation regime, as the density of active ionized impurities. \( N \) values for all samples are reported in the sixth column of table 1. Errors correspond to standard deviation of the above-mentioned average.

The concentration of bulk contaminants activated during our fabrication processes is not directly the \( N \) value, since we have to consider the starting doping level of the material. In the most frequent case, an n-type sample is contaminated and becomes p-type. The amount of acceptors \( N_a \) needed for this is the sum of the starting n-type dopant concentration \( (N_{\text{growth}}) \) to be compensated, plus \( N \) positive carriers that are measured, i.e. \( N_c = N + N_{\text{growth}} \). All possible combinations of starting and final dopant concentration can be described by the formula:

\[
N_c = |(\pm) N - (\pm) N_{\text{growth}}|
\]  

using the + sign for p-type dopant and − for n type.

Growth impurity densities \( N_{\text{growth}} \) are taken from the impurity level \( (N \text{ values}) \) of reference samples Rn and Rp, equal to \( 8.7 \times 10^9 \) cm\(^{-3} \) for Rn and \( 8.9 \times 10^9 \) cm\(^{-3} \) for Rp. The concentration of thermally-induced acceptor defects \( N_a \) is reported in table 1, for each sample.

Looking at the \( N_c \) column in detail, it can be seen that B ion implantation is a clean process as expected, since it does not introduce any further contaminant into HPGe. A really remarkable result is obtained with laser thermal annealing of Sb (LTA sample): its impurity level is fully compatible with the starting material level. This means that this doping...
The technique does not introduce shallow levels inside HPGe, as also confirmed by the measurement of the carrier type, that remains n-type after the process.

Regarding the SiO$_2$ coating (CAP sample), it has not provided any protective action since the underlying bulk is contaminated even more than a naked sample that had received the same annealing treatment. Samples coated with SOD sources (P1, P2 and Ga) are characterized by the same (or even less) impurity density as other as-cut samples that received a similar annealing treatment (T1, T3 and T6 respectively). This means that the SOD film does not introduce further impurities inside Ge. The same is true for the Sb sample, doped by diffusion from a remote source.

It is interesting to look at the sample treated inside a different furnace (T7), because it turns out to have a higher impurity density than T3 and P2 annealed with very similar temperature ramps. This could suggest that active doping species under study are not intrinsically present inside HPGe or formed during the process and then activated during the annealing, but probably they are impurities coming from the external environment and diffusing inside HPGe during the thermal treatment. The difference in contaminant level could be due to different levels of quartz chamber purity, induced by previously performed treatments in the same apparatus or by intrinsic material quality, or it could be due to a variability in the sample surface contamination during sample preparation. We have to consider that one thousandth of monolayer can provide the contaminant amount necessary to reach the measured levels. More investigations should be performed about this point to draw certain conclusions.

Anyway, the most evident behavior emerging from the observation of $N_c$ values in table 1 is that the concentration of doping defects increases by moving to higher thermal budgets.

### 3.3. Phenomenological model of contamination process

The contamination of the HPGe crystal may occur because of the diffusion of external contaminants or because of the formation of intrinsic defects under annealing (dislocations multiplication, point defects clustering, etc).

A phenomenological model has been created that allows to explain the contamination process under furnace annealing. In a first step we considered the pure thermal effect as the only cause of contamination. Samples coated with SOD sources (P1, P2 and Ga) are characterized by the same (or even less) impurity density as other as-cut samples that received a similar annealing treatment (T1, T3 and T6 respectively). This means that the SOD film does not introduce further impurities inside Ge. The same is true for the Sb sample, doped by diffusion from a remote source.

It is interesting to look at the sample treated inside a different furnace (T7), because it turns out to have a higher impurity density than T3 and P2 annealed with very similar temperature ramps. This could suggest that active doping species under study are not intrinsically present inside HPGe or formed during the process and then activated during the annealing, but probably they are impurities coming from the external environment and diffusing inside HPGe during the thermal treatment. The difference in contaminant level could be due to different levels of quartz chamber purity, induced by previously performed treatments in the same apparatus or by intrinsic material quality, or it could be due to a variability in the sample surface contamination during sample preparation. We have to consider that one thousandth of monolayer can provide the contaminant amount necessary to reach the measured levels. More investigations should be performed about this point to draw certain conclusions.

Anyway, the most evident behavior emerging from the observation of $N_c$ values in table 1 is that the concentration of doping defects increases by moving to higher thermal budgets.
where the dependence of $T$ on time is explicitly expressed. The integration of equation (7) over time returns:

$$n = r \cdot n_0 \int \exp\left(-\frac{E_{\text{act}}}{k_B T(t)}\right) dt.$$  

Equation (8) can be used to model the contamination data $N_c$ as a function of the thermal treatment ramp $T(t)$, once given the parameters $r \cdot n_0$ and $E_{\text{act}}$. In order to facilitate the model calibration, we introduce the quantity $TB$ (thermal budget) as the integral term in equation (8):

$$TB = \int \exp\left(-\frac{E_{\text{act}}}{k_B T(t)}\right) dt.$$  

$TB$ can be computed for each process (once the activation energy has been fixed) by using the function $T(t)$ that was registered through a thermocouple during each furnace treatment. It is worth to note that such number summarizes the effect of a thermally activated process during a general thermal history, including heating and cooling ramps that may be significant for short annealing times.

In figure 4 the plot of $\exp\left(-\frac{E_{\text{act}}}{k_B T(t)}\right)$, for one peculiar value of activation energy (2.1 eV), is shown for all fast-annealing treatments. Thermal budgets are calculated as the integral of these curves.

In order to facilitate the fitting and to take into account the large dynamics of the contamination data, we apply the natural logarithm to equation (8), getting a linear relation between $\ln(n)$ and $\ln(TB)$:

$$\ln(n) = \ln(r \cdot n_0) + \ln(TB).$$  

This last equation can be used to fit our experimental data, particularly those done in the same furnace, using $E_{\text{act}}$ and $r \cdot n_0$ as free parameters. We tested possible values of $E_{\text{act}}$ in the range from 0.6 to 3 eV. Once calculated the thermal budgets of all the annealing treatments performed in the furnace (i.e. those of samples P1, P2, Ga, Sb, CAP, T1, T2, T3, T4, T5, T6), it was possible to create a plot $\ln(n)$ versus $\ln(TB)$, where each point refers to a single sample. Points should lie on a straight line with a slope equal to 1, according to equation (10).

In figure 5(a), groups of points corresponding to different values of activation energy are reported. Each group was fitted with a linear function, by keeping the slope fixed to 1. In figure 5(b), the mean square deviation (MSD) between data and the fit is plotted for the different activation energies. The minimum MSD determines the best possible value for the activation energy $E_{\text{act}} = (2.1 \pm 0.1)$ eV. The corresponding $r \cdot n_0$ value is $2.1 \times 1021$ cm$^{-3}$ s$^{-1}$.

In figure 6, the best fit is reported, i.e. with 2.1 eV activation energy. As can be noted, the model with only two free parameters allows to order the data in a well-defined trend. The mean square relative displacement of each datum from the fit is 34%. This is a very good result considering that the data set comes from very different annealing procedures: temperatures from 600 °C to 800 °C, times from 2 to 30 min and different shapes of the temperature ramp. We can surely state that the thermal budget is the main parameter that causes the contamination.

In order to understand if the average displacement hides some systematic dependence on other experimental parameters, we divided the data in different subsets and inspected the trend with respect to the average model. In figure 6(a) we divided the data on the basis of the type of starting bulk, either p or n. This could be in principle an important parameter, since p and n specimens are generally taken from different zones of the ingot and may have in principle different grown-in defects. Both starting bulk types seem to be homogeneously distributed around the fitting line. This suggests that the contamination process is independent of the starting substrate type. In figure 6(b) we divided the sample in etched and not etched surface. It can be noted that there is a clear correlation between the impurity density and surface removal, namely etched samples present a lower impurity level. This indicates that the first micrometers of material are more contaminated and confirms that contaminants come from the external environment and diffuse inside Ge during high temperature annealing. Thus, most likely, they are extrinsic, in-diffusing contaminants. This excludes all those species that, already
present inside bulk HPGe, could be electrically activated during the annealing by forming complexes with other impurities or defects [14]. By exploiting the theoretical estimates of [2], the role of intrinsic point defects in the phenomenon can be further ruled out if one considers that the concentration of vacancies that can form during thermal treatment at 810 °C or 610 °C is less than $4 \cdot 10^9$ cm$^{-3}$ and $4 \cdot 10^6$ cm$^{-3}$ respectively, for an intrinsic or p-type doped Ge. These numbers are orders of magnitude less than the measured contamination levels of our samples (about $10^{14}$ cm$^{-3}$ and $10^{11}$ cm$^{-3}$ respectively at the two temperatures), and they become even lower if interstitials are considered despite of their higher formation energy with respect to vacancies [4].

In figure 6(c) SOD-coated and not-coated samples are divided. This is in principle a fundamental step since we would like to answer the question if SOD is responsible for contamination. As a matter of fact, samples with SOD have a lower contamination density. This can hardly be attributed to a protective effect of SOD, since the SiO$_2$ coating has not proved to be an effective barrier towards contaminant diffusion. More likely, the lower contamination density can be attributed to the fact that SOD-covered samples are all surface etched. Thus, since there is not a direct correlation between the presence of the SOD source during the annealing and the contamination process, the remarkable conclusion is that the SOD film does not introduce further contaminants.

By considering the p nature of the shallow dopant and also its origin (i.e. the external environment), it could be identified with copper. Several proofs point to this identification: Cu is one of the fastest diffusing impurities in Ge. Moreover, substitutional Cu atoms give rise to three acceptor levels in Ge and this is compatible with the p nature of active impurities. According to Bracht et al [15], Cu diffusion $D^{\text{eff}}_{\text{Cu}}$ and solubility $C_{\text{Cu}}^{\text{s}}$ in highly dislocated Ge (as our samples are, about 2000 cm$^{-2}$) are given by:

$$D^{\text{eff}}_{\text{Cu}} = \left(7.8 \times 10^{-4}\right) \exp \left(-0.084 \text{eV}/(k_B T)\right) \text{ cm}^2 \text{s}^{-1}$$

$$C_{\text{Cu}}^{\text{s}} = \left(3.44 \times 10^{23}\right) \exp \left(-1.56 \text{eV}/(k_B T)\right) \text{ cm}^{-3}.$$  

The two activation energies needed for Cu atoms to diffuse inside Ge and reach the substitutional solubility are, respectively, 0.084 eV and 1.56 eV. In order to contaminate the material, Cu has to be both solubilized and diffused into the Ge.
Therefore, by substituting (15) into (14) we get:

$$L^2 = D_0 \exp \left(-E_{\text{act}} / (k_B T)\right) t.$$  \hfill (15)

If the temperature $T$ varies during the process, i.e. it is a function of time (as it happens in fast treatments) equation (15) can be directly generalized as follows:

$$L^2 = D_0 \int \exp \left(-E_{\text{act}} / (k_B T(t))\right) dt.$$  \hfill (16)

The last integral was defined as the thermal budget of the annealing treatment. By applying the natural logarithm to the equation, we achieve a linear relation:

$$\ln (L^2) = \ln (D_0) + \ln (TB).$$  \hfill (17)

Equation (17) was used to fit diffusion length data in the same way as equation (10) was used for bulk contamination process. In figure 7 we report the best fit result for P and Sb. In the case of P diffusion, the best fitting was obtained with an activation energy of $(2.4 \pm 0.1) \text{ eV}$, and $D_0 = 113.7 \text{ cm}^2 \text{s}^{-1}$. In the case of Sb diffusion, the activation energy is $(2.7 \pm 0.1) \text{ eV}$, and $D_0 = 148.6 \text{ cm}^2 \text{s}^{-1}$.

On the basis of this result it is possible to identify, if it exists, an optimal range for thermal budgets, which allows dopant diffusion inside HPGe without contaminating. We fixed an upper acceptable limit for contamination of $n^\text{thr} = 2 \times 10^{10} \text{ cm}^{-3}$. According to equations (8) and (9), in order to respect this threshold, $TB$ should be limited by:

$$TB < \left(n_c^{\text{thr}} / (rn_0)\right).$$  \hfill (18a)

For simplicity, if we consider a step-like treatment, with $T$ temperature for a time $t$ (no ramps), equation (18a) becomes:

$$t \exp \left(-E_{\text{act}} / (k_B T)\right) \leq \left(n_c^{\text{thr}} / (rn_0)\right).$$  \hfill (18b)

By rearranging equation (18b), we get the maximum acceptable annealing time at a given temperature to have a contamination lower than $n_c^{\text{thr}}$:

$$t \leq n_c^{\text{thr}} / ((rn_0) \exp ((E_{\text{act}} / (k_B T))).$$  \hfill (19)

In other words, by applying the natural logarithm to Equation (19), it defines a line in the $t$ versus $1/(k_B T)$ plane that separates non-contaminating thermal budgets from the contaminating ones (continuous line in figure 8). A similar reasoning can be done to impose a minimum P and Sb diffusion threshold into HPGe starting from equation (16). Particularly, a threshold $L_0 = 200 \text{ nm}$ for dopant diffusion length is set, in order to ensure the formation of a continuous and homogeneously-doped contact layer. We easily obtain a formula for the minimum time needed to have such doping depth:

$$t > L_0^2 / (D_0 \exp ((E_{\text{act}} / (k_B T))).$$  \hfill (20)

By applying the natural logarithm to equation (20), it defines a line in the $t$ versus $1/(k_B T)$ plane that separates sufficient thermal budgets from the insufficient ones to obtain a 200nm thick doped layer. In figure 8 the dashed line corresponds to
P diffusion threshold, while the dotted one corresponds to Sb diffusion threshold.

As can be observed, within the time and temperature range reachable with a standard tube furnace, it is not possible to find an optimal thermal window. In fact, a thick P- or Sb-doped layer cannot be obtained without contaminating the bulk HPGe, since lines do not cross. Anyway, by working with shorter times thus moving gradually towards a state of out-of-equilibrium, the onset of large thermal gradients within the material could allow to achieve good dopant diffusion while keeping the impurity density below the established threshold. Thus, a more rapid annealing technique that operates in the range of milliseconds, such as flash lamp annealing (FLA) [29], could be more appropriate for these purposes. The situation would change completely by moving to Ge melting temperature (938 °C), which can be done through LTA technique. In melted Ge, dopants diffuse orders of magnitude faster than in solid, therefore the solid-state diffusion expressed by Sb and P diffusion lines completely changes. Besides, this technique acts just on the first hundreds of nanometers of material, leaving completely unheated the bulk. In this way, the process of bulk contamination should be negligible. We have had a first evidence of this by characterizing the n-type HPGe sample that had received LTA of sputtered Sb. The functionality of such process to build working HPGe diodes is demonstrated in [12].

4. Conclusions

In this work the results of the characterization of the amount of electrically active defects found inside HPGe, after high temperature annealing treatments in standard furnaces, have been presented. Through electrical measurements at low temperature, we measured the density of these doping defects and their sign. Their density turned out to be higher when high thermal budgets were applied and the shallow levels introduced were acceptor type. The phenomenon was studied in samples that had received different annealing treatments, different surface doping processes and also different surface treatments. Taking into account the electrical features of these active defects and the fact that they have a higher concentration in the first 10 µm of the surface, we concluded that most likely we are dealing with copper atoms coming from the external environment.

It is worth to note that both SOD and Sb doping can be exploited by keeping a level of contamination less than 10^{12} cm^{-3}. While this level is not suitable for γ-ray detectors that work at low temperature, it is clearly good for all other room temperature applications: since thermal carriers in Ge at 300 K are 2 × 10^{13} cm^{-3}, any doping below such value cannot modify the carrier concentration of devices. On the other hand, bulk contaminant behavior as recombination traps should be evaluated. We also conceived an empirical model for the dependence of impurity density on the applied thermal budget. The model is an innovative framework that can be used to evaluate contamination effects in any application where high thermal budget process may be needed. In the specific case of HPGe, the obtained activation energy of (2.1 ± 0.1) eV for the contamination process was compared to the activation energies of (2.4 ± 0.1) eV and (2.7 ± 0.1) eV for P and Sb diffusion. Hence, those values were used to set thresholds for minimum P and Sb diffusion and maximum bulk contamination, in order to find a possible thermal window for non-contaminating doping processes in HPGe. However, in the range of temperatures and times reachable with an equilibrium annealing technique such a window of allowed thermal budgets does not exist.

It is evident from our results that this optimal window should be sought for shorter times, entering a regime of strongly out-of-equilibrium thermal processes and, what is most important, annealing should be limited to the Ge surface, keeping the bulk as cold as possible. FLA and LTA could be suitable techniques to reach these conditions. A first evidence of LTA effectiveness has already been demonstrated in this work and this approach turns out to be the most promising and concrete perspective to renew and improve doping processes in HPGe materials.

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