STEM analysis of deformation and B distribution in nanosecond laser ultra-doped Si$_{1-x}$B$_x$

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Abstract

We report on the structural properties of highly B-doped silicon (up to 10 at.% of active doping) realised by nanosecond laser doping. The crystalline quality, lattice deformation and B distribution profile of the doped layer are investigated by scanning transmission electron microscopy followed by high-angle annular dark field contrast studies and geometrical phase analysis, and compared to the results of secondary ions mass spectrometry and Hall measurements. When increasing the active B concentration above 4 at.%, the fully strained, perfectly crystalline, Si:B layer starts showing dislocations and stacking faults. These only disappear around 8 at.% when the Si:B layer is well accommodated to the substrate. With increasing B incorporation, an increasing number of small precipitates is observed, together with filaments with a higher active B concentration and stacking faults. At the highest concentrations studied, large precipitates form, related to the decrease of active B concentration. The structural information, defect type and concentration, and active B distribution are connected to the initial increase and subsequent gradual loss of superconductivity.

Keywords: STEM, dopant distribution, nanosecond laser doping, ultra-doped silicon, B aggregates

(Some figures may appear in colour only in the online journal)

1. Introduction: why study ultra-doped silicon?

When silicon is strongly doped with boron (>6 × 10$^{20}$ cm$^{-3}$), a superconducting phase appears in this covalent material [1–3]. To understand the mechanisms leading to the onset and evolution of superconductivity, the knowledge of the structural properties and of the boron distribution and activation is essential. Moreover, superconducting silicon devices are emerging [4, 5], that need, to be designed and developed, such information on the homogeneity and activation of the doping. To achieve extremely high doping, we employ an out of equilibrium technique, nanosecond laser doping, necessary to overcome the solubility limit (~4 × 10$^{20}$ cm$^{-3}$) and to incorporate up to 10 at.% (5 × 10$^{21}$ cm$^{-3}$) of electrically active B atoms [6, 7]. Due to the technical difficulties of achieving such high doping levels, ultra-doped Si is still generally badly known. The largest contributions come from extensive studies of boron-implanted silicon treated by an excimer laser annealing (ELA), whose crystalline properties [8, 9] and mechanisms of dopant redistribution and aggregation [10] are reported [4]. As opposed to these ultra-doped layers fabricated by ion implantation and nanosecond laser annealing, gas immersion laser doping (GILD) introduces the dopants with a (softer) chemisorption, followed by nanosecond laser anneal under ultra high vacuum (UHV). GILD samples will thus be exempt from the deep structural defects induced by the implantation,
and their crystalline quality may outperform that of ELA samples.

In this paper, we discuss the results of an experimental study performed by STEM (scanning transmission electron microscopy), SIMS (secondary ion mass spectrometry) and transport Hall measurements on Si:B layers with doping in the range \( \times 10^{-18} \text{ cm}^{-3} \)–\( \times 10^{21} \text{ cm}^{-3} \) range realised by GILD.

When progressively increasing the doping, an initial linear increase of the hole carrier density is measured by Hall effect (i.e. active B concentration, \( n_B \text{ Hall} \)), followed by a slower non-linear increase and a decrease at higher doping (figure 1(b)). For the same samples, the superconducting critical temperature was measured from resistance vs. temperature curves in an adiabatic demagnetisation refrigerator. The values reported in figure 1, corresponding to the temperature where the resistance is reduced to 50% of its normal state value, show that the superconducting critical temperature increases to a maximum corresponding to the maximum of the active B concentration, and then decreases when the active concentration decreases. We thus expect the B active concentration to be a determining parameter for superconductivity. The aim of this paper is to show in this article, for series with different laser fluences. We show in this article deformation or the high angle annular dark field (HAADF) intensity, with comments on the precision and limitations of these analysis.

2. Ultra-doping: GILD

GILD \([11, 12]\) is performed in a ultra high vacuum reactor (\( \sim 10^{-9} \text{ mbar} \)) which insures a very low impurity level. A puff of the boron precursor gas, pure BCl\(_3\), is injected using a pulse valve onto the (100) oriented high resistivity n-type silicon surface to induce a pressure of \( \sim 10^{-5} \text{ mbar} \), just enough to saturate the chemisorption sites (figure 1(a)). As the gas is continuously pumped, photolytic or pyrolytic chemical vapor deposition (CVD) processes are avoided, and the supplied quantity of dopant atoms, from the chemisorbed layer, is constant and self-limited. After a small delay, a pulse of an excimer XeCl laser (\( \lambda = 308 \mu \text{m} \) with pulse duration 25 ns) is sent to the sample area and absorbed over \( \sim 7 \text{ nm} \). Given the electron-phonon characteristic time, the light energy can be considered as completely and instantly converted into thermal energy. The heat produced is evacuated very quickly (87 \( \text{mm}^2 \text{ s}^{-2} \)) by one-dimensional diffusion to the substrate (in 25 ns the heat diffuses over about \( 1 \mu \text{m} \)). The thermal energy melts the silicon from its surface, the silicon melting threshold being 600 mJ cm\(^{-2}\). The greater the amount of laser energy absorbed, the deeper the melting front advances in the substrate. Thus, the density of laser energy is proportional to the doped thickness. All chemical species diffuse in the liquid. Once the thermal energy is dissipated in the substrate and the local temperature decreases below the melting temperature, an epitaxial recrystallization front rises to the surface at a speed of about 4 \( \text{m s}^{-1} \) \([14]\), slow enough for the crystal to reconstruct from the underlying crystal lattice in the absence of defects (epitaxy) and fast enough to trap in substitutional sites the boron atoms with a segregation coefficient close to 1, achieving concentrations larger than the solubility limit. When the crystallization front reaches the surface, the excess impurities contained in the liquid are expelled outwards, such as Cl whose segregation coefficient is close to 0 \([13]\). To improve the uniformity of the 2 mm \( \times 2 \text{ mm} \) laser spots, and thus achieve a straight interface between the doped layer and the substrate, the spatial inhomogeneity of the laser energy density is reduced to about 1% by a careful optical treatment of the laser beam using, in particular, a fly-eye homogenizer (a system composed of two squares 11 \( \times 11 \) micro lens matrices).

This entire chemisorption-melting-crystallisation process can be repeated the desired number of times (number of laser shots \( N \)) to increase the overall concentration of dopants in a single layer, as shown in figure 1(b).

3. Measuring the Si:B structure and the B distribution

Several GILD samples were prepared with laser fluencies in the range \( E = 756–1070 \text{ mJ cm}^{-2} \) and a number of shots in the range \( N = 1–950 \). The evolution with doping is comparable for series with different laser fluences. We show in this article
a detailed analysis of several samples made with a fixed laser fluence of 1070 mJ cm\(^{-2}\) (corresponding to a 176 nm thick layer) and a varying number of shots \(N = 1\)–\(N = 950\) (corresponding to hole concentrations from \(5.5 \times 10^{18} \text{ cm}^{-3}\) to \(4.3 \times 10^{21} \text{ cm}^{-3}\)). We present the sample analysis results for \(N = 200\) laser shots (linear regime), \(N = 350\) and \(N = 700\) (non-linear regime), and \(N = 950\) shots (decreasing regime). The doped layer thickness has been measured by STEM to 176 nm, and corresponds to the beginning of the out-of-plane deformation rise, which is clearly visible on the contrast bright field images. This value was confirmed by SIMS within the measurement uncertainty estimated to ±5 nm.

### 3.1. STEM Analysis

The technical details concerning the STEM measurements are specified in the section 6. STEM observations enable us a precise analysis of the crystalline quality of the Si:B layer epitaxial on the Si substrate. Crystalline defects such as dislocations or stacking faults can thus be observed. In this work, we will present only the images obtained in HAADF mode (figure 2).

In addition, on the same images, geometrical phase analysis (GPA), an analysis in the Fourier space, [15, 16] is performed which provides a powerful tool to measure the deformations quantitatively (figure 3). The Si:B layer in-plane deformation (\(\varepsilon_\|\)) and out-of-plane deformation (\(\varepsilon_\perp\)) are thus measured in relation to the Si substrate:

\[
\varepsilon_\| = \frac{a_{\text{SiB}} - a_{\text{Si}}}{a_{\text{Si}}} \quad \varepsilon_\perp = \frac{a_{\text{SiB}} - a_{\text{Si}}}{a_{\text{Si}}} \tag{1}
\]

where \(a_{\text{Si}} = 0.5431\) nm.

### 3.2. Extraction of the B distribution profile

The concentration profiles cannot be directly extracted from STEM to EDX (energy dispersive x-ray) analysis since the energy of the \(K\alpha\) ray of the B is too close to the L\(\alpha\) line of the Si (spectrum figure 4(a)). In addition, the peak intensity \(I_{\text{K\alpha}}\) is very low. We will nevertheless benefit from EDX to estimate qualitatively the evolution of the layer concentration at the highest doping. The dopant profiles are instead extracted in two ways, either through the lattice deformation only (GPA), or through both the lattice deformation and the HAADF contrast.

In the first case, we exploit Vegard’s law, stating that in a binary compound, the lattice parameter is directly related to the composition by:

\[
\alpha_{\text{SiB}} = n_{\text{B}}\% \alpha_{\text{B}} + (1 - n_{\text{B}}\%)\alpha_{\text{Si}}. \tag{2}
\]

To extract the Si:B lattice parameter in the hypothesis of an isotropic material, one can use Si Poisson coefficient to relate the perpendicular and parallel deformations measured by GPA. The resulting concentration is given by:

\[
n_{\text{B \ Vegard}}(\%) = \frac{a_{\text{Si}}}{(1 - K)(a_{\text{B}} - a_{\text{Si}})}(K\varepsilon - \varepsilon_\perp) \tag{3}
\]

where \(K = -\frac{2\nu}{(1-\nu)} = -0.77\) for the silicon value \(\nu = 0.278\). Further details on equation (3) are given in the section 6. As equation (3) shows, to extract \(n_{\text{B \ Vegard}}\) it is necessary to assume a value for the lattice parameter of B, \(a_{\text{B}}\), in a cubic lattice, which is not the case. In the literature, values range from \(a_{\text{B}} = 0.378\) nm [17] to \(a_{\text{B}} = 0.4084\) nm [18]. Thus, \(a_{\text{B}}\) and the Si:B Poisson coefficient \(\nu\) are the main sources of uncertainty in the derivation of the substitutional B concentration profile from the lattice in-plane and out-of-plane deformations.

HAADF images can also be exploited to deduce the B concentration profile. Indeed, the high angular integrated intensity is directly related to the atomic number \(Z\) of the atomic columns scanned by the electron probe [19]. If we assume that in the binary compound Si:B, all the B atoms replace Si atoms in the crystal lattice, and that there are not other elements present, it is theoretically possible to calculate the B concentration from the deformation and the HAADF contrast, defined as the ratio between the layer intensity (\(I_{\text{SiB}}\)) relative to the volume of Si:B crystal lattice (\(V_{\text{SiB}}\)) and the substrate intensity (\(I_{\text{Si}}\)) relative to the volume of the Si crystal lattice (\(V_{\text{Si}}\)):

\[
C_{\text{HAADF}} = \frac{I_{\text{SiB}}}{I_{\text{Si}}/V_{\text{Si}}} \tag{4}
\]

The B percent atomic concentration, \(n_{\text{B \ HAADF}}\), is given by equation (5) (see also section 6 for further details)

\[
n_{\text{B \ HAADF}}(\%) = \left[\frac{(1 - \varepsilon_\perp)(1 - \varepsilon_\|)C_{\text{HAADF}} - 1}{Z_B^7 - Z_{\text{Si}}^7}\right]^{\frac{1}{3}}. \tag{5}
\]

We stress that this expression applies to monocrystalline layers without defects or impurities.

### 3.3. SIMS analysis

SIMS analysis was performed by taking special care to the quantification of B doping for the studied concentrations, higher than \(10^{21} \text{ cm}^{-3}\). In particular, an oxygen primary beam was employed to correct the matrix effects, and only secondary ions at high energy (>100 eV) were analysed as they are less sensitive to the chemical surrounding (see section 6 for further details). This technique makes it possible to quantify the total amount of B (\(n_{\text{B \ SIMS}}\)) present in the doped layer regardless of his position in the crystal.

### 3.4. Hall transport measurements

The hole concentration was measured by Hall transport on the same spots analysed by STEM. Hall measurements were performed on a Hall cross etched on each spot with a central region 300 \(\mu\text{m} \times 300 \mu\text{m}\). The influence of the substrate is negligible due to the n–p barrier between the p-type layer and the n-type substrate. The hole concentration is directly related to the active B concentration as each B atom provides a hole carrier:

\[
n_{\text{B \ Hall}} = \gamma \frac{1}{dqR_{\text{H}}} \tag{6}
\]
Figure 2. STEM–HAADF images of the doped layer with (a) \( N = 200 \), (b) \( N = 350 \), (c) \( N = 700 \) and (d) \( N = 950 \) shots. The FFT of each image on the Si:B part gives indications on the crystal quality. On the \( N = 350 \), \( N = 700 \) and \( N = 950 \) shots images, the inserts are focused on the crystal defects (stacking faults and dislocations with burgers vector determination) or on the precipitates.

where \( q \) is the electron charge, \( d \) is the thickness of doped layer, \( R_H \) is the Hall coefficient measured from the slope of the linear \( V_H/I \) (B). \( \gamma = 0.75 \) [20] is the Hall mobility factor, the ratio between the Hall mobility \( \mu_H \) and the conductivity mobility \( \mu_c \): \( \gamma = \mu_H/\mu_c \). The main uncertainty on \( n_{BH} \) is related to the Hall mobility factor, which varies in the literature between
4. Results and discussions

In the following part, we describe the Si:B layer properties in the three regimes of active B evolution with the number of laser shots $N$ (linear increase, non-linear increase and decrease, see figure 1). For each regime the results from all the characterisation methods employed are commented: STEM–HAADF images, to observe the crystalline quality of the layer, its structural defects, and B precipitates (figure 2); GPA analysis, to observe the in-plane and out-of-plane lattice deformation (figure 3); STEM–EDX images to compare the amount of B in the layer and in the precipitates (figure 4); the B overall concentration and concentration profile extracted from SIMS, Hall, and/or STEM analysis through Vegard’s law or HAADF contrast, to observe the dopant homogeneity and accumulation (figure 5).

4.1. Linear regime

A characteristic example of the behaviour at the far end of the linear regime is the 200 laser shots sample. The Si:B layer presents the same crystal lattice quality as the Si substrate (figure 2(a)) with no defects. The inset fast Fourier transform (FFT) pattern reveals an epitaxial orientation relationship (cube-on-cube) between the two lattices.

Figure 3(a) shows that the crystal lattice of the Si:B layer is tensile strained, with an out-of-plane deformation $\varepsilon_\perp$ roughly constant within the layer, varying from $\varepsilon_\perp = -1.4\%$ in the 35 nm above the Si:B/Si interface, to $\varepsilon_\perp = 0.7\%$ at the surface (table 1). No in-plane deformation $\varepsilon_{\parallel}$ is observed. This is as expected when the doping is low enough that a monocrystalline Si:B layer can be epitaxied without defects on the underneath Si substrate through elastic relaxation. Indeed, due to the epitaxial relation with the substrate, the in-plane lattice constant is equal to the Si one while the out-of-plane lattice constant is reduced to accommodate for the smaller lattice volume due to the smaller B size.

$\gamma = 0.7$ and $\gamma = 0.8$, and whose value was either calculated or extrapolated from measurements below $n_B = 10^{21}$ cm$^{-3}$.

Figure 3. STEM–HAADF images of the doped layer with (a) $N = 200$, (b) $N = 350$, (c) $N = 700$ and (d) $N = 950$ shots. Below each HAADF image, are represented the out-of-plane and in-plane deformation maps with the averaged profiles.
Table 1. Summary of some deformation’s values measured by GPA analysis and B concentration measured or calculated by different methods (SIMS, Hall measurements, Vegard’s law, \(C_{\text{HAADF}}\)). The thickness values of the different sublayers were taken from the interfaces determined from the deformation profiles (3rd line) measured in GPA (figure 2). The concentration values found in SIMS or calculated from HAADF contrast reported correspond to the average of the concentration in the thus determined layers.

|                      | \(N = 200\) | \(N = 350\) | \(N = 700\) | \(N = 950\) |
|----------------------|--------------|--------------|--------------|--------------|
|                      | SiB layer    | SiB/Si interface | SiB layer    | SiB/Si interface | SiB layer    | SiB/Si interface | SiB layer    |
| **GPA deformation**  |              |              |              |              |              |              |              |
| \(\varepsilon_{\perp}\) (%) | 176          | 15           | 35           | 124          | 5            | 12           | 67 studied    | 10           | 15           | 115 studied |
| \(\varepsilon_{\parallel}\) (%) | 0            | 0            | 0            | 0            | 0            | 0            | 0            | 0            | 0            | 0            | 0            | 0            | 0            |
| **\(n_B\) (cm\(^{-3}\) \times 10^{21}\)** |              |              |              |              |              |              |              |              |              |              |              |              |              |
| HALL                 | 1.7          | 2.60         | 4.04         | 3.86         |
| Vegard law with high aB | 1.6 \(\gamma\) 1.1 | 1.5          | 3.1          | 2.8 \(\gamma\) 2.3 | 1.1          | 3.3          | 4.2          | \(\gamma\) 1.7 | 3.5    | 3.8          |
| Vegard law with low aB | 1.3 \(\gamma\) 0.9 | 1.2          | 2.6          | 2.1 \(\gamma\) 1.7 | 0.9          | 2.7          | 3.5          | \(\gamma\) 2.1 | 4.3    | 4.65         |
| \(C_{\text{HAADF}}\) |              |              |              |              |              |              |              |              |              |              |              |              |              |
| SIMS                 | 2.3 \(\gamma\) 1.9 | 3.50         | 3.3          | 6.7          | 6.1          | 6.6          | 10.8 max     | 6.6          |         |              |

**SiB layer type deformation** | **Elastic deformation** | **Elastoplastic deformation** | **Plastic deformation** | **Twinning-mediated plastic deformation**
Figure 4. STEM–EDX (a) spectra, (c) and (d) respectively B and Si mappings corresponding at the HAADF image (b) on a Si:B layer with 950 shots. On the spectra, the C and O peaks are due to surface contamination of the FIB section, the Ga peak is due to the preparation of the thin lamella with a Ga$^+$ ions beam, the presence of the Cu peak is due to the fluorescence on the TEM grid.

From the deformation profile, the concentration profile of the active, substitutional B is extracted with equation (3) ($n_B$\textsubscript{vegard}). The profiles thus obtained with $a_B$ in the range given by literature (figure 5(a), blue lines) show $n_B$\textsubscript{vegard} = 1.6 \times 10^{21}$ cm$^{-3}$ constant over approximately 40 nm above the Si:B/Si interface, followed by a roughly linear decrease down to 1.05 \times 10^{21}$ cm$^{-3}$ at the surface. The value obtained by Hall measurements, $n_B$\textsubscript{Hall}, also sensitive only to active, substitutional B atoms, confirms this value: $n_B$\textsubscript{Hall}–$n_B$\textsubscript{vegard}, the agreement being particularly good in the bottom 40 nm. The SIMS profile $n_B$\textsubscript{SIMS}, sensitive instead to the total amount of B, is similar but with higher values of concentration, $n_B$\textsubscript{SIMS} = 2.3 \times 10^{21}$ cm$^{-3}$ near the interface to $n_B$\textsubscript{SIMS} = 1.9 \times 10^{21}$ cm$^{-3}$ near the surface (figure 5(a) green line). The difference between $n_B$\textsubscript{SIMS} and $n_B$\textsubscript{vegard} is possibly due to the presence of non-electrically active B $n_B$\textsubscript{inactive} = $n_B$\textsubscript{SIMS} – $n_B$\textsubscript{vegard}. Even though SIMS, Hall measurements and the deformation all draw a coherent picture, HAADF is puzzling. Indeed, we observe a HAADF contrast $C_{HAADF}$ > 1: the intensity of the Si:B layer is larger than that of the substrate (figure 3(a)), while we would expect $C_{HAADF}$ < 1 for substitutional B atoms equation (4) since $Z_B$ (=5) < $Z_{Si}$ (=28). It is thus impossible to calculate the concentration profile B by equation (5). This gives an indication that another phenomenon is masking the replacement of Si atoms by B atoms in the crystal lattice, such as the presence of substitutional atoms with a larger Z than the Si, such as Cl atoms from the precursor gas. However, the EDX spectra on all the Si:B layers do not show any other elements. The most likely hypothesis is the homogeneous and significant presence of Si interstitial atoms. It is unclear how to explain such important presence of interstitial Si. Note that the same results were obtained for a second lamella on the same spot and in other spots at doping $N$ =350.

4.2. Non-linear regime

When increasing the doping to attain the non-linear regime, (characterised here by the $N$ = 350 laser shots sample) we observe the appearance of dislocations at the Si:B/Si interface and the propagation of stacking faults in the thickness of the layer that show the beginning of plastic relaxation (figure 2(b)). These stacking faults and dislocations also appear in the inset FFT pattern as tilted lines connecting the diffraction spots, as well as in the GPA charts (figure 3(b)). At the Si:B/Si interface, we observe a fully strained 15 nm layer with $\varepsilon_{\perp}$ = –1.3% and $\varepsilon_{\parallel}$ = 0 (figure 3(b)). On top of this layer, a second layer of about 35 nm shows the maximum $\varepsilon_{\perp}$ = –2.6% with a weak in plane deformation of $\varepsilon_{\parallel}$ = –0.5%. The dislocations start from the bottom of these
two layers. Finally, the rest of the Si:B layer (124 nm) has a roughly constant $\varepsilon_\parallel = -0.7\%$ and $\varepsilon_\perp$ increasing to $-2\%$.

Indeed, the doping is too high to build a fully strained, monocrystalline layer, and three layers form within the doped region: the first just above the Si substrate, fully strained, correspond to a low doping concentration at the interface ($1.5 \times 10^{21}$ cm$^{-3}$), the second sees the doping increasing to the concentration of the liquid phase ($\sim 3 \times 10^{21}$ cm$^{-3}$) and presents the maximum out-of-plane deformation while the in-plane is small but not strictly zero anymore, while the last layer to crystallize is partially relaxed, with an increasing in-plane deformation and a decreasing out-of-plane deformation when proceeding upwards. An intermediate regime elastoplastic is observed.

Figure 5(b) (blue lines) shows the substitutional B concentration profile extracted with Vegard’s law. We observe $n_{B \text{vegar}} = 2.6 \times 10^{21}$ cm$^{-3}$ over approximately 35 nm above the first strained, low doping, layer. Note that the areas where the dislocations and amorphous precipitates are present are not analysed by the GPA software, and thus do not contribute to the deformation signal. The extraction of the dopants profile from the lattice deformation through Vegard’s law is thus validated, as confirmed by the good agreement with Hall measurements. The SIMS profile (figure 5(a), green line) gives as before a total concentration larger than the Hall/Vegard’s one with a similar profile. Reasoning as for $N = 200$, the difference between $n_{B \text{SIMS}}$ and the active B concentration is interpreted as indication of inactive B. As expected, we find a monotonically increasing inactive B concentration with doping when calculating $n_{B \text{SIMS}} - n_{B \text{vegar}}$, smaller for $N = 350$ than $N = 200$. A possible interpretation is that, at $N = 200$, the deformation is sensitive to the amount of interstitial Si (assumed to explain the $C_{\text{HAADF}} > 1$), preventing a quantitative extraction of $n_{B \text{Vegard}}$ for $N = 200$. This may also be true for $N = 350$, to a lesser extent. Indeed, for $N = 350$ as for $N = 200$, the HAADF contrast is $>1$ in the upper 150 nm of the layer. In the bottom layer, the expected HAADF contrast $<1$ is found, which however does not allow to extract a reasonable B concentration ($4.6 \times 10^{21}$ cm$^{-3}$), possibly due to a distortion caused by small precipitates.

At $N = 700$ shots (figure 2(c)), the end of the non-linear regime is reached. HAADF images show dislocations near the Si:B/Si interface, and we recover a good crystalline quality in the doped layer, similar to that of the untreated substrate, with no stacking faults. The Si:B layer has thus well accommodated its lattice on the substrate by plastic deformation. The insert FFT pattern is similar to the one obtained on the sample images with $N = 200$. As before, the formation of multiple layers (figure 3(c)) is observed. The first, at the interface, is fully strained, with a small out-of-plane deformation over 5 nm and corresponds to the doping decrease at the end of the Si:B
layer when B active concentration is about $1.1 \times 10^{21}$ cm$^{-3}$. The second, 12 nm thick, is also fully strained ($\varepsilon_\perp = 0$) but presents a large out-of-plane deformation $\varepsilon_\parallel = -3.3\%$ (corresponding to $n_B \sim 3.3 \times 10^{21}$ cm$^{-3}$). Above these two layers the in-plane deformation increases sharply until $\varepsilon_\parallel \sim -2.1\%$, and we observe small dark areas corresponding to small precipitates and misfit dislocations identified by their Burger vector $1/2a_{Si}$ (110) (Lomer loops). The rest of the layer is nearly fully relaxed with $\varepsilon_\parallel \sim -2.2\%$ and a similar $\varepsilon_\perp = -2\%$. The active B concentration is then $\sim 4.2 \times 10^{21}$ cm$^{-3}$.

On the HAADF image (figure 2(c)), we can also notice column-shaped regions spanning up to the thickness of the layer, of dark contrast and therefore less rich in Si. Presumably they are richer in B. This may be explained as a beginning of the cellular breakdown process [21], where the liquid–solid interface roughness leads to lateral impurities segregation with respect to the main solidification front, and forms crystalline twinned structures where a large dopant concentration can be found in substitutional sites [22].

On figure 5(c) (blue lines), the B concentration profile obtained by the Vegard’s law shows an almost constant value on the first 80 nm of the Si:B layer from the interface. These values are in good agreement (between 89 and 92% depending on $n_B$) with the Hall effect measurement. The concentration measured by SIMS (figure 5(c), green line) is about 34% higher than $n_B$ \textit{Vegard} or $n_B$ \textit{Hall}. The difference between the SIMS profile and Vegard’s profile is explained as inactive B atoms that do not participate to the deformation of the Si:B lattice. The larger quantity of inactive B as compared to $N = 350$ follows the expected evolution. An increase of the inactive B concentration at the Si:B/Si interface (peak in $n_B$ \textit{SIMS} while $n_B$ \textit{Vegard} is nearly constant), present also at $N = 350$, may be associated to the small precipitates observed by HAADF (figure 2(c)).

The profile $n_B$ \textit{HAADF} obtained from $C_{HAADF}$ by equation (5) corresponds to the profile given by the Vegard’s law and the Hall measurement value in the layer $\sim 40$ nm above the interface. On the other hand, at the interface the concentration extracted from the HAADF is larger than the expected, with $n_B$ \textit{HAADF} $\sim n_B$ \textit{Vegard} due to the effect of the small precipitates. This is confirmed by the similar profiles of SIMS and HAADF at the bottom of the layer.

### 4.3. Decreasing regime

Finally, the highest B concentration studied ($N = 950$ shots) shows a decrease of the active concentration. Large black areas are observed in HAADF contrast at the Si:B/Si interface. An EDX map (figures 4(b)–(d)) of the layer shows that in these dark areas the lack of Si corresponds to B accumulation (spectrum figure 4(a), purple line). These B precipitates are amorphous since the crystallinity is lost in the FFT. Large ($> 30$ nm) micro maculated areas extend from these precipitates towards the surface (figure 2(d)). Their signature is also visible on the FFT pattern as extra points (FFT figure 2(d)). Furthermore, small precipitates through the layer are observed (black dots in figure 2(d)). They are incoherent with the Si matrix, since the Burger vector is zero, indicating the absence of global dislocations (i.e. zoom figure 2(d)).

Similar to the previous samples, the layer presents three sub-layers (figure 3(d)). The first, $\sim 10$ nm thick, is fully strained with $\varepsilon_\perp$ increasing to $\varepsilon_\perp = -2.5\%$ and no in-plane deformation. The second, $\sim 15$ nm thick, is partially relaxed with $\varepsilon_\perp = -2.8\%$ and $\varepsilon_\parallel$ increasing up to $\varepsilon_\parallel = -2\%$, while the third, fully relaxed layer shows $\varepsilon_\perp$ slowly decreasing up to $\varepsilon_\perp = -2\%$ and $\varepsilon_\parallel$ increasing in two steps to $\varepsilon_\parallel = -1.9\%$ and $-2.1\%$.

On figure 4(d) blue line, after the 40 first nanometres, the B concentration calculated with the Vegard’s law is almost uniform and is in good agreement (between 98% and 83% depending on $n_B$) with the Hall measurement. The value calculated with the $C_{HAADF}$ is much higher than the Vegard’s value (41%) which suggests that the HAADF contrast is distorted by the presence of the many small precipitates in the layer and the large precipitates mostly found at the interface (see the peak in the HAADF) and in the thickness of the layer.

### 5. Conclusions

Through complementary analyses (STEM HAADF–GPA, SIMS, Hall), we investigate the phenomena that occur when B concentrations as high as $n_B \sim 10$ at.% are incorporated into $\langle 100 \rangle$ silicon by nanosecond laser doping. At B concentrations lower than $n_B \sim 2$ at.%, active B varies linearly with the number of laser shots. This is expected from the constant incorporation of dopants at each laser shot, determined by the self-limited precursor gas concentration chemisorbed at the sample’s surface. In this case, the totality of B is found in substitutional positions in the Si crystal lattice. At $n_B = 4.3$ at.%, the Si:B layer presents an elastic relaxation in the growth plane that does not induce crystalline defects, forming a fully strained layer with deformation up to $\varepsilon_\perp = -1.4\%$. SIMS analysis gives a higher concentration than that obtained by the Vegard’s law or by Hall measurement: at $n_B \sim 3$ at.%, 15% of the incorporated B is electrically inactive and does not participate in the deformation of the crystalline lattice. Moreover, an amount of interstitial Si needs to be assumed to understand the STEM–HAADF analyses, while no other contamination was detected by STEM–EDX at the detection limit (0.1 at.%). Between 4.3 at.% and 8 at.%, the increase in active B concentration gradually slows down with the number of laser shots, while the inactive B concentration grows to 34%. We observe the beginning of a plastic relaxation with the formation a fully strained sublayer $\sim 15$ nm thick at the Si:B/Si interface and a partially relaxed sublayer on top, with increasing deformation in and perpendicular to the layer plane. This incomplete relaxation generates many crystalline defects, such as dislocations and stacking faults in the layer. We also still observe a small amount of interstitial Si above the thin fully strained layer. Surprisingly, superconductivity appears in this relaxed, defected phase. At the end of the non-linear regime, around
8 at.% active B, the plastic relaxation is complete: the lattice crystal is well accommodated to the substrate with only localized misfit dislocations in the sublayer above the fully strained sublayer. At this interface, few B precipitates begin to appear. We also observe inhomogeneities in the active B concentration as filaments starting from the interface with the fully strained layer possibly related to cellular breakdown processes. According to the HAADF contrast there is no more Si in interstitial positions. When the number of shots is increased further, the concentration of active B decreases. Above the 10 nm thick strained layer, the lattice is completely relaxed, and B creates large precipitates mostly at the interface between fully strained and relaxed layers, and a few precipitates in the layer. The STEM observation of a N = 950 shots sample shows that the lattice crystal is completely at fault with large twinned domains. A crystalline disorder sets in, which decreases the electrical and in turn the superconductive performances. It should be also noted that despite the uncertainty linked to the parameter $a_B$ which varies in the literature by $\sim 8\%$, the calculation of the active B concentration profile with the deformations measured by STEM–GPA and the Vegard’s law is consistent with the values measured by Hall effect. The calculation seems to give better results if we adopt a smaller $a_B$ for disturbed regimes with many dislocations and stacking faults ($N = 350$: start of plastic relaxation and $N = 950$) and a larger $a_B$ for stable regimes without crystalline defects in the Si:B layer ($N = 200$: elastic relaxation and $N = 700$: plastic relaxation). Obtaining the B concentration profile by studying the HAADF contrast is possible (i.e. $N = 700$) but the presence of interstitial impurities and B precipitates disturbs the contrast.

6. Methods/technical details

6.1 STEM analysis

For the STEM analysis, a thin lamella (<100 nm) is machined vertically in the laser-doped spot thanks to a focus ion beam using a FEI ThermoFisher SCIOS dual beam SEM (UHR NiCol)/FIB (Siderwinder 550 V–30 kV) with an in-situ easy-lift micromanipulator. All samples were observed in an aberration-corrected FEI ThermoFisher TEM/STEM TitanThemis 200 operating at 200 kV. The convergence half-angle of the probe was 17.6 mrad and the detection inner and outer half-angles for HAADF–STEM were 69 mrad and 200 mrad, respectively. The lamella was imaged along the 1 1 0/zone axis. All micrographs where 2048 by 2048 pixels. The dwell time was 8 µs and the total acquisition time 41 s. GPA is performed in Digital Micrograph software on STEM–HAADF images. EDX measurements were performed in the Titan microscope featuring the Chemistem system, that uses a Bruker windowless Super-X four-quadrant detector and has a collection angle of 0.8 sr. The acquisition time for the mappings was 10 min, during which no significant drift occurred. This analysis allows us to know the elements present in the sample at a concentration greater than or equal to 0.1 at.%.

6.2. SIMS analysis

SIMS measurements were performed with a 4F Cameca system equipped with a magnetic mass spectrometer. For doping levels above $5 \times 10^{20}$ cm$^{-3}$, the doping value can be difficult to extract due to matrix effects. However, it was shown that using an oxygen primary beam, the variation of the relative ion yield is the same for B and Si, so that the matrix effect can be corrected by the comparison with the silicon signal and using the relative sensibility factor [12]. Moreover, only the secondary ions at high energy (>100 eV) were used for the analysis, as they are less sensitive to the chemical surrounding. Boron concentration is then obtained by comparison with a standard from the National Institute of Standards. Depth calibration is obtained with a mechanical profilometer and we consider the sputter rate difference between the doped layer and the silicon substrate.

6.3. Extraction of the dopant profile

6.3.1. Vegard’s law. It is possible to calculate the profile of the B concentration from the GPA measurements. Indeed, in a binary compound, the lattice parameter is directly related to the composition by the Vegard’s law equation (2),

$$a_{SiB} = n_{B\%} a_B + (1 - n_{B\%}) a_{Si} \quad (7)$$

$$n_B (\%) = \frac{a_{SiB} - a_{Si}}{a_B - a_{Si}}.$$

In an isotropic material, the perpendicular deformation is related to the parallel deformation by the Poisson coefficient:

$$\frac{a_{SiB\perp} - a_{SiB}}{a_{SiB}} = K \frac{a_{SiB\parallel} - a_{Si}}{a_{SiB}}$$

with $K = -\frac{2}{1 + \nu} = -0.77$ if we adopt the Poisson coefficient of Si ($\nu = 0.278$) which however may evolve in Si:B at higher concentrations,

$$a_{SiB} = K a_{SiB\perp} - K a_{SiB}\parallel \frac{1}{1 - K}.$$

Thus, starting from the deformations measured through the GPA (equation (1)), it is possible to extract $a_{Si:B}$ then $n_B$ though equation (3):

$$n_{B\text{Vegar}} (\%) = \frac{a_{Si}}{(1 - K) (a_B - a_{Si})} \left( K \varepsilon \parallel - \varepsilon \perp \right). \quad (8)$$

6.3.2. HAADF contrast. The HAADF contrast is defined as the ratio between the intensity of the layer ($I_{SiB}$) relative to the volume of Si:B crystal lattice ($V_{SiB}$) and the intensity of the substrate ($I_{Si}$) relative to the volume of Si crystal lattice ($V_{Si}$) (equation (4)),

$$C_{HAADF} = \frac{I_{SiB}/V_{SiB}}{I_{Si}/V_{Si}}. \quad (9)$$
The integrated intensities are proportional to the atomic number \( Z \) at power 1.7 \([12]\) and the volume of the Si:B lattice depends on the deformations measured in GPA.

\[
I_{SB} \propto x_B Z_B^{7} + (1 - x_B) Z_s^{7}
\]

\[
I_{SL} \propto Z_s^{7}
\]

\[
V_{SB} = a_B^3 (1 - \varepsilon_{\perp}) (1 - \varepsilon_{||})^2
\]

\[
V_{Sl} = a_s^3
\]

where the deformations of the two in plane directions are considered equal.

Thus, the B percent atomic concentration, \( n_B \), can finally be calculated by:

\[
n_{BHAADF} (%) = \left[ \frac{(1 - \varepsilon_{\perp})(1 - \varepsilon_{||})C_{HAADF}}{Z_B^7 - Z_s^7} \right] \cdot (10)
\]

**Data availability statement**

The data that support the findings of this study are available upon reasonable request from the authors.

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