Lattice contraction due to boron doping in silicon

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ABSTRACT

In modern electronic devices, strain is used to increase carrier mobility. It is thus mandatory to know precisely the effect of doping on the lattice parameter of silicon. However, there are many experimental biases which prevent one from measuring this effect with high accuracy. For this reason, we have designed and fabricated a step-like structure consisting of five 50 nm-thick Si layers of increasing substitutional boron concentrations. Then, we have used Dark Field Electron Holography, a Transmission Electron Microscopy based technique, to measure the strain in these pseudomorphic and defect-free layers. Using Finite Element Modelling, we show that the observed out-of-plane strains can be reproduced by assuming that the expansion coefficient of boron is about -6.5×10^{-24} cm^3. This value is slightly larger (in absolute value) than those previously reported. It is otherwise about 20% larger than predicted from the size mismatch between B and Si atoms.

Strain is today an integral feature of modern electronic devices. Indeed, the mechanical deformation of the crystalline lattice modifies the effective mass, the scattering, and consequently the mobility of charge carriers in semiconductors [1]. This principle is being extensively applied to boost the performance of Si and Ge based devices by introducing strain of desired amplitude and direction in the channel region of metal-oxide-semiconductor field-effect transistors [2–4]. There are several different possible technological routes to implement this strain, from the deposition of intrinsically stressed layers such as SiN and TiN to the engineering of sources and drains of different lattice parameters. In the latter case, the short channel region is confined between the two strained pockets and deforms to an equilibrium (strained) configuration which can be predicted using Finite Element Modelling (FEM).

To engineer this strain, source and drain regions can eventually be built of epitaxial alloys such as silicon-carbon (Si$_x$ C$_{1-x}$)[5–8] and silicon-germanium (Si$_x$ Ge$_{1-x}$) [9–12] of various compositions that have lattice parameters different (smaller and larger, respectively) from those of the Si matrix. The relations between C or Ge concentrations and resulting lattice parameters are well established [13,14]. However, these regions have to be heavily doped. The dopant atoms being of different sizes than the host Si atoms, this substitution will also result in a change of its lattice parameter. Thus, the final characteristics of the channel will also depend on the dopant concentrations in the source and drain regions. The fine tuning of strain in the channel of modern devices thus requires that the impact of doping on the lattice parameter of Si is also precisely established.

Boron being the classical p-type dopant of Si, one might think that the relation between B concentration and lattice parameter is known since decades. Surprisingly, as it will be shown latter in this letter, this is not the case. In general, it is noted that the substitution of silicon by boron atoms results in a contraction of the lattice. In theory, the change of lattice parameter should linearly depend on the boron concentration through β, the expansion coefficient. The simplest approach consists in attributing this change to the difference of atomic radii between the host (Si) and the substitutional impurity atoms (B). This is known as the Vergard's law for solid solutions. For boron in silicon, this leads to an expansion coefficient β of about -5.46×10^{-24} cm^3 (atomic radii from [15]). Actually, a second mechanism may play a role through electronic interactions (deformation potentials) [16], enhancing or reducing the size mismatch effect. A spectacular example of the effect of deformation potentials is that of As, which expands more the Ge lattice than the Si lattice [17].

However, the relation between boron concentration and change of the lattice parameter is often found to be not linear, the contraction appearing proportionally smaller for high boron concentrations. This characteristic evidences the difficulties of running clear cut experiments in that field. Indeed, there are a number of biases which should be avoided to establish an accurate relation between dopant concentration and lattice parameter. Firstly, all impurity atoms should be dopants i.e., they must only sit on substitutional sites and consequently be electrically active. Indeed, inactive boron occupies interstitial sites, alone or in clusters, and tend to strain the Si lattice in the opposite direction i.e., towards a larger lattice parameter. This will mask the contraction effect due to substitutional doping. Secondly, the doped silicon crystal should be defect-free, with no dislocations or Boron Interstitials Clusters

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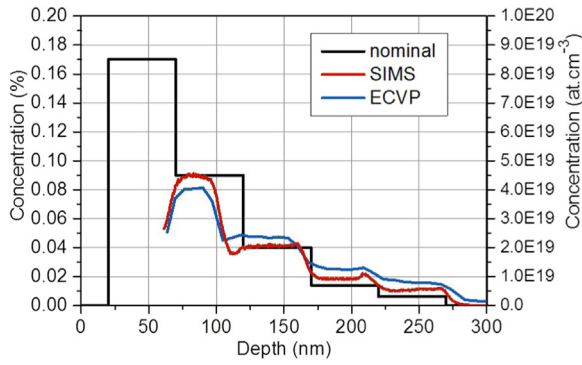 E-mail address: claverie@cemes.fr (A. Claverie).

Fig. 1. Boron concentration profiles measured by SIMS and ECVP in the stacked structure plotted together with the nominal concentrations measured by four probes resistivity on full sheet companion samples.

(BICs). Finally, the doped silicon should be homogeneous, as expected for a solid solution. Thus, appropriate samples are hard to fabricate, which probably explains the disagreement between published reports. In this work, we have specially designed and fabricated a sample of high purity and used a combination of experimental techniques to avoid these biases.

A 200 mm Si(100) sample consisting of a stack of five 50 nm-thick doped Si layers of increasing boron concentrations, from 3×10^{18} to 8.5×10^{19} at cm^{-3}, was grown by Reduced Pressure – Chemical Vapor Deposition (RP-CVD) in an AMAT Epi Centura 5200 reactor at 650 °C under conditions favoring the incorporation of boron atoms on substitutional sites during growth (i.e., at 20 Torr with SiH$_4$, B$_2$H$_6$ and high amounts of ultra-pure H$_2$ as a carrier gas [18]). The doping concentrations were measured by four probes resistivity on companion samples grown as single doped layers under the very same conditions. The stack was finally covered by a 20 nm thick undoped Si layer. The atomic boron concentration depth profile was measured by Secondary Ions Mass Spectroscopy (SIMS) while the carrier concentration depth profile was measured using Electrochemical Capacitance-Voltage Profiling (ECVP) [19]. Fig. 1 shows the results of these measurements.

For the 4 layers up to a concentration of 4.5×10^{19} B cm^{-3}, the SIMS and EVCP profiles are in very good agreement and very close to the nominal concentrations, within $\pm\, 2 \times 10^{18}$ B cm^{-3}. This shows that almost all (if not all) the boron atoms are on substitutional sites in these layers. Close to the surface, both the SIMS and the ECVP

techniques show different artifacts which prevent us from absolute comparison. For this layer, we assume that the doping concentration is that obtained from resistivity measurements.

The change in lattice parameter due to doping of the epitaxial layers leads to in-plane stress in the pseudomorphically grown films. In reaction, the films shrink in the perpendicular direction (out-of-plane strain) by an amount that is determined by the local doping concentration and by the elastic constant of Si, through the Poisson's law. In general, these out-of-plane lattice spacing are measured by x-ray diffraction on separate samples. In our work, we have used Dark Field Electron Holography (DFEH) to measure these deformations on the same sample. DFEH is a recently invented Transmission Electron Microscopy (TEM) based interferometry technique able to map strain with a high precision (2.10^{-4} in this work) and nanometer resolution (5 nm in this work) over micrometers wide fields of view [10,20]. In short, two highly coherent electron waves diffracted respectively by a reference (unstrained) zone and the region of interest are forced to interfere in the image plane and form a hologram. The Fourier analysis of these holograms allows one to extract the phase shifts between these waves from which strain along the diffraction direction can be retrieved. By changing the diffraction vector used for imaging, strain can be explored along all directions of the image plane. For details of the technique, the reader is referred to the book chapter by Hÿtch et al. [21].

Fig. 2.a is a map of the in-plane strain observed in our sample. The inset shows the integrated profile of this image along z, the depth into the sample. Neither strain nor defects can be detected in the structure confirming that the layers were pseudomorphically grown on the Si substrate.

Fig. 2.b is a map of the out-of-plane strain. From the substrate, the image tends to get greenish as the layers contain more boron. Again, the inset shows the integrated profile of this image along the z direction. It clearly shows that strain increases from the substrate towards the Si cap layer at the surface.

We now aim at extracting the expansion coefficient from the comparison of FEM simulations with our DFEH measurements. The model first needs to describe our structure as a stack of five pseudomorphic 50 nm-thick layers of different relaxed lattice parameters. These lattice parameters are linearly related to the local concentrations of boron through the relation:

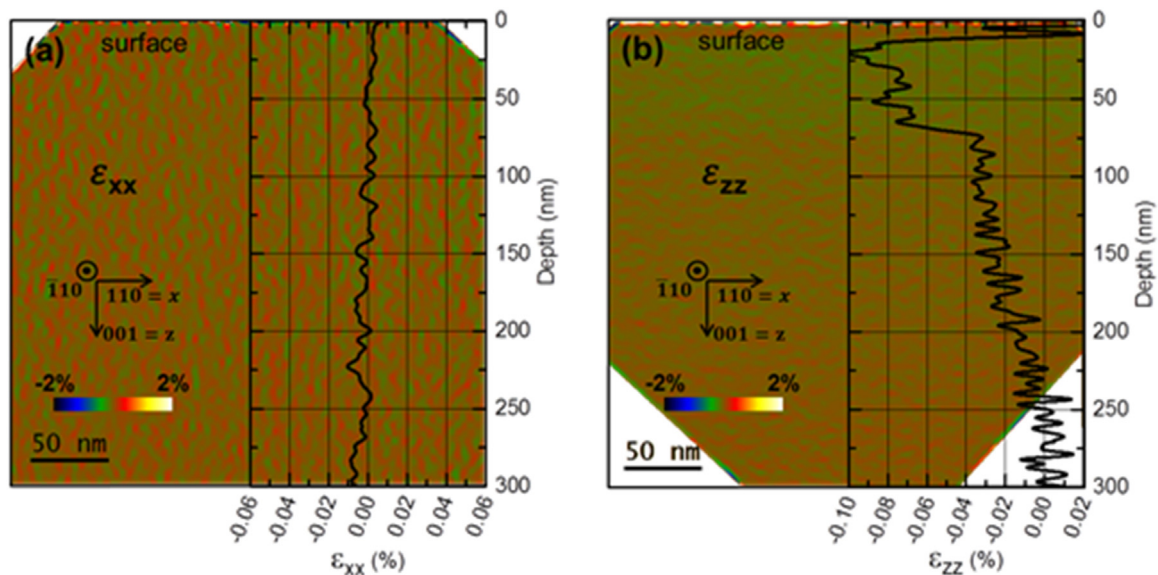$$\frac{a_{Si:B} - a_{Si}}{a_{Si}} = \beta . N_B,$$

Fig. 2. (a), in-plane (ε_{xx}) and (b), out-of-plane (ε_{zz}) strain maps measured by DFEH. The insets show the integrated strain profiles along the depth of the sample.
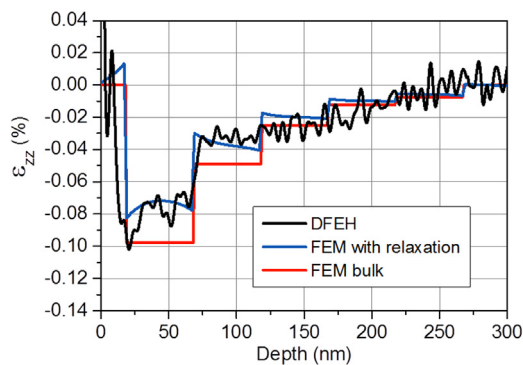
Fig. 3. Out-of-plane strain profile (ε_{zz}) of the sample, along the z direction, measured by DFEH (in black) and reproduced by FEM; in red, considering neither the relaxation of the thin foil nor the oscillations of the diffracted wave and, in blue, taking into account these effects.
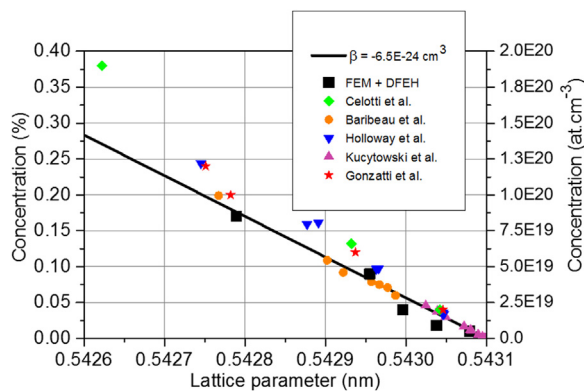

Fig. 4. Plot of the B concentration versus the lattice parameter of Si:B from our results (black line and black squares) and several results found in the literature: Celotti et al. [23], Baribeau et al. [24], Holloway et al. [25], Kucytowski et al. [26] and Gonzatti et al. [18].

where $a_{Si:B}$ is the lattice parameter of silicon doped with a boron concentration of N_B, a_{Si} is the regular lattice parameter of Si and β the so-called expansion coefficient. In the four first layers, the local boron concentrations are taken as the means between the SIMS and ECVP values shown in Fig. 1 and as 8.5×10^{19} B cm^{-3} in the last layer, as obtained from resistivity measurements.

The specimen used for TEM imaging being much thinner (90 nm) than the overall structure, some relaxation of the structure occurs in the thin foil. This is also included in the FEM as well as the effect resulting from the oscillation of the wave amplitude of the diffracted beam during its propagation through the thickness of the specimen [22]. Finally, the value of β which allows for the best fitting of the overall experimental strain profile, shown in Fig. 3, is extracted from the model with an accuracy estimated to be of about $+/-5\%$.

β is found to be -6.5×10^{-24} cm^3. Clearly, the effect of strain relaxation in the thin lamella is important and therefore must be taken into account. Moreover, it is interesting to note that the strain gradients observed within the doped layers only result from the relaxation of the thin foil and not from any doping concentration gradient. However, this explains why the different doping "steps" are not easily and individually imaged by DFEH.

We have reported our results along with several results found in the literature in Fig. 4. The lattice expansion coefficient β we have found suitable to reproduce the whole set of out-of-plane strains measured in our sample is plotted as a straight black line. The black squares are obtained when reproducing individually at best each of the differently doped Si layers. For literature data, we have kept only those results for which the boron concentrations were clearly below the solid solubility

limit of boron at the process temperature and for which some evidence was provided that boron atoms were electrically active. Some authors have directly measured β. Celotti et al. [23] deduced a value of -4.6×10^{-24} cm^3, Baribeau et al. [24] -6.2×10^{-24} cm^3, Holloway et al. [25] -5.19×10^{-24} cm^3 and Kucytowski et al. [26] -5.9×10^{-24} cm^3. We could infer a β value of -5.8×10^{-24} cm^3 for Gonzatti et al. [18]. Looking at Fig. 4, one can see that we have obtained an expansion coefficient close to but slightly larger, in absolute value, than those previously reported. In other words, we show that the incorporation of boron in silicon contracts the lattice parameter slightly more than previously thought.

One possible reason for this slight discrepancy may arise from different impurity contents in the samples. Indeed, most impurities such as metals, incorporated during the sample fabrication process (epitaxial growth or ion implantation), lie on interstitial sites and thus contribute to some local increase of the lattice parameter, resulting in some underestimation of the contraction effect due to boron doping. In contrast, the RP-CVD technique used in this work is an industrial process well-known for fabricating high purity silicon based materials suitable for advanced microelectronics. We believe this can explain some discrepancy with older results. Another reason may be that, in some cases and especially at high B concentrations, not all the boron atoms occupies substitutional sites, for example when its concentration is obviously above the solid solubility limit at the process temperature. The presence of boron in interstitial positions, alone or within clusters easily detectable by TEM [27] would also have a counter effect and would lead one to underestimate the contraction effect of boron doping. Lastly, the doped layers should be really pseudomorphic on bulk relaxed Si i.e., no extended defects should be present in the region of the sample probed for strain measurement. DFEH being a TEM based technique, these two biases have been avoided in this work. The strain measurements we have obtained originate from regions of the sample which are defect-free guaranteed.

In summary, we have designed and fabricated a step-like structure consisting of five Si layers of increasing boron concentrations. We have checked that all the incorporated boron was electrically active i.e., on substitutional sites. Then, we have used DFEH to measure the out-of-plane strain in these layers. Being a TEM based technique, it allowed us to verify that the probed regions were defect-free and pseudomorphic. Using FEM, we have shown that we could reproduce the observed out-of-plane strain by assuming that the expansion coefficient of boron was about -6.5×10^{-24} cm^3. This value is close to but slightly larger (in absolute value) than those previously reported and about 20% larger than predicted from the size mismatch between B and Si atoms.

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