Investigation of boron implantation into silicon by quantitative energy-filtered transmission electron microscopy

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Abstract. High-resolution electron microscopy (HREM), chemical mapping by energy-filtered transmission electron microscopy (EFTEM), electron energy-loss spectroscopy (EELS) and energy-loss spectroscopic profiling (ELSP), also called spectroscopic transverse image profiling by EFTEM (stripeTEM) have been combined to study the distribution of boron after implantation into silicon at low energy (0.5keV) and rapid thermal annealing. The key to the experiments is that stripeTEM combines both ~1nm spatial resolution and sub-at% sensitivity. It is shown that the near-surface spike of boron visible in secondary ion mass spectrometry (SIMS) profiles is an artefact of surface profiling. The real distribution of boron is several nm deeper into the specimen, in agreement with both Monte Carlo simulations and shoulders apparent in the SIMS profile. Quantification of the experimental stripeTEM data shows that the B concentration is approximately ~2at% in the SiO

1. Introduction

For electronic devices doping of layers at specific depths in silicon (Si) wafers is commonly established by ion implantation, and a suitable p-dopant is boron (B). A subsequent anneal is then used to ensure that, firstly, the implanted ions move from interstitial to lattice sites so they become electrically active, and, secondly, other point and also more extended lattice defects produced during the implantation are effectively healed out [1].

2. Implantation, anneal, SIMS measurements and Monte Carlo simulations

The Si wafer investigated was first pre-amorphised using 12 keV Ge, co-implanted with 7keV C (at a dose of 1×10

15 cm

2

) and then doped using carborane implantation [2] to give an implant equivalent to 0.5keV B at a dose of 1×10

15 cm

2

. A rapid thermal anneal at 1025°C was performed for a few seconds to re-grow the crystal and activate the boron. Si interstitials released during the crystal re-growth can lead to transient enhanced diffusion and clustering of B interstitials [2].

The post anneal boron depth distribution was measured by secondary ion mass spectroscopy (SIMS) profiling. Fig. 1 shows the SIMS result, with an apparent peak at just ~1nm below the surface and two broader peaks at ~4nm and ~12nm depths. Fig. 2 depicts the predicted profile for the as-
implanted boron from Monte Carlo simulations using the SRIM code [3], which predicts an ion range of ~4nm, in agreement with an extrapolation from values tabulated for higher ion energies [4]. This suggests that the 4nm and 12nm peaks are due to the as-implanted profile and transient enhanced diffusion during the anneal. A previous transmission electron microscopy (TEM) study on a higher dose and energy boron only implant [5] suggested that the surface peak in the post anneal profile could be an artefact of the SIMS technique. The aim of this study is to investigate this further for a case that included amorphisation and co-implants, and see if any evidence of B clustering could be observed.

**Figure 1.** SIMS depth profile of B distribution

**Figure 2.** Monte Carlo simulation of B implantation into Si/SiO$_2$ [3].

### 3. TEM Experiments

**Figure 3.** Cross-sectional elastic bright field (BF) image formed by using a slit aperture in the energy-dispersive plane to exclude all inelastic scattering. The top of the implanted Si shows diffraction contrast due to strain.

**Figure 4.** High-resolution electron microscopy along [100] zone axis with {022} lattice fringes of 0.19nm spacing in Si. The top left depicts the amorphous glue, then follow the Cr layer (dark), native SiO$_2$ (speckle contrast) and the Si substrate (grey) at the bottom right.

A stripe of 30mm x 3mm was cleaved from the wafer piece provided and a ~3nm Cr layer was evaporated on top of it to seal and define the surface for later analysis. Then a piece was glued together with a SiGe multi-layer sample as reference for both magnification and analytical signals, the stack was backed by more pieces of Si, cut along <100> directions using a wire saw, ground, mechanically polished and finally milled until perforation by argon ions at 3keV energy, 3mA combined current from top and bottom surface, ~15° angle of incidence and 2kV sample bias.
The sample was then investigated near [100] zone axis orientation in a JEOL 2010F field-emission gun transmission electron microscope (FEG-TEM) equipped with a Gatan Imaging Filter (GIF) operated at 197-200 kV acceleration voltage. The methods applied were bright-field imaging (BF), high-resolution imaging (HREM), energy-filtered imaging (EFTEM) and energy-loss spectroscopic profiling (ELSP). Figures 3 and 4 show the structure in cross-section at medium and high resolution, respectively. Below the 2 nm SiO$_2$ layer there is a clear indication for a 2-3 nm wide band of darker contrast in the top of the crystalline Si.

The chromium layer is 2.6±0.1 nm wide and delineates the former free surface which has been ion implanted. The Cr layer has actually been partially oxidized in air, as shown in Figs. 5e and f. The native oxide layer thickness has been determined to be 2.1±0.2 nm. A ~0.8 nm thick layer of strongly varying contrast has been observed within the top 2 nm of silicon, indicating strain contrast, presumably due to numerous point defects. Depending on orientation and focus settings, this strained layer may appear bright or dark (see figure 3). No extended lattice defects or precipitates have been observed, however, and the silicon lattice seems intact everywhere else.

Energy-filtered imaging and electron energy-loss spectroscopic profiling indicate the presence of a sub-nm thin layer buried ~2 nm under the Si/SiO$_2$ interface which is completely invisible in HREM. It only shows up as a faint dark line in EFTEM at energy losses between the Si L-edge and the B K-edge and ratio images calculated from those (shown in Fig. 6c), but these are impossible to quantify. While ratio and three-window imaging techniques consistently indicate a B rich layer in the Si, multiple window background fitting to an extended series of energy filtered images acquired with 5 eV slit width from 150 eV to 225 eV reveals the presence of small B-rich clusters ~0.3 nm thick and up to 1 nm in length, positioned ~4 nm below the original wafer surface which has been marked by a line in Fig. 6d, however, the analysis is now complicated by the oxide layers becoming unstable under the electron beam and changing structure as a function of time, thereby producing spurious artefacts in the form of larger patches of alternating bright and contrast at the position of the oxide layers in Fig. 6d.

![Figure 5](image.png)

**Figure 5.** Results from energy-filtered imaging. (a) is a relative thickness map obtained from the ratio of inelastic to elastic scattering. The max. thickness near the image top is ~0.65 times the inelastic mean free path in the Si, which is ~125 nm at the imaging conditions chosen, while the sample thickness is only 0.13 times the mean free path near to the Si/SiO$_2$ interface. The elemental distribution maps (b-f) have been calculated for the corresponding energy-loss core-loss edges using the standard 3-window-method and inverse power-law background fitting and subtraction. These maps show the presence of the corresponding elements (the more the lighter the image).
Energy-loss spectroscopic profiling allows us to extract electron energy-loss spectra (EELS) of the Si L-edge commencing at 99eV and the B K-edge commencing at nominally 188eV, at the positions of interest with ~1nm spatial resolution in the growth direction. Quantification of these is rather difficult. For the Si this is due to the general uncertainty in the scattering cross-sections of L-edges and for the B it is due to the weakness of the signal (i.e. smaller inelastic scattering cross-section plus lower concentration). The quantification procedure was as described in [6, 7]:

- vertical interpolation of spectroscopic images by factor 2 (vertical stretching) to 0.23nm/line
- cross-correlation of images at specimen edge to eliminate relative drift along the vertical
- line-by-line EELS data extraction from spectroscopic images
- EELS background fit (inverse power law)
- background subtraction
- signal integration over 70eV (Si), 50eV (B, C) or 30eV (O) from edge onset, note: no de-convolution has been applied; B K-edge commences at ~195eV, higher than literature values (188eV) suggest
- normalisation for different exposure times and scattering cross-sections
- plot of profiles
- ratio of boron signal to sum over signals from all major elements yields atomic concentration

An evaluation of the relative edge intensities taking into account the different cross-sections consistently yields values between 2at% and 4at% B if the integration range chosen is at least 30eV wide (integration windows only 20eV wide or smaller positioned directly after the edge onset yield erroneous results due to the delayed nature of the Si L-edge and possibly a slight energy drift). Fig. 7 is a patchwork of such electron energy-loss spectroscopic profiles that display intensity as a function of growth direction upwards and as energy loss horizontally. The dispersion along the horizontal direction is 0.103eV/channel, the original sampling along the vertical direction is 0.46nm/pixel. The Cr signal defines the surface, and EEL spectra shown in Figs. 8 and 9 have been extracted from lines corresponding to the positions of the SiO$_2$ and the Si near the clusters observed. Taking into account the different scattering cross-sections B concentrations of 2.6 and 4.0at% are calculated, respectively, with statistical errors of about ±0.2at% due to noise and background fitting and systematic errors of 0.6at% due to uncertainties in the scattering cross-sections necessary for scaling the electron intensities measured. These values are close to the detection limit of the technique.

Figure 6. Multiple-window energy spectroscopic imaging (ESI) has revealed B-rich clusters ~6.5nm below the surface of the Cr layer, i.e. ~4nm deep under the surface the original (oxidised) wafer (d). They are located where in energy-filtered imaging just before the B K-edge at 188eV a dark layer is observed within the Si (a, b), and ratio imaging suggests additional contrast due this edge (c) but cannot be quantified. Above the line drawn in (d) the B map only shows noise, just below it the SiO$_2$ is unstable and yields artefacts, but the bright regions that are also bright in (c) indicate a few B clusters in the form of thin platelets.
Figure 8. Si (left) and B (right) electron energy-loss spectra (EELS) extracted from the SiO$_2$ region (10s exposures). The ratio of Si/B=11.8±0.9 implies a boron concentration of 2.6±0.2at% within the SiO$_2$. Turquoise/grey are experimental spectra, red the background fits, dark blue the theoretical cross-sections from Hartree-Slater theory and green the extracted edges. No de-convolution was applied because the sample was sufficiently thin ($t/\lambda=0.10$) to neglect plural inelastic scattering.
The ratio of Si/B = 23.9 ± 1.1 implies a boron concentration of 4.0 ± 0.2 at%. 

Figure 9. Si and B EELS from the Si near the dark region in Fig. 2 where the B clusters were observed (10s). The ratio of Si/B = 23.9 ± 1.1 implies a boron concentration of 4.0 ± 0.2 at%. $\delta = 0.13$

Figure 10. Quantitative B profile extracted from the stripe TEM data in Figs. 7c and 7d

Finally, the boron concentration profile along the growth direction shown in Fig. 10 was extracted from the B and Si spectra. Values that correspond to positions in the glue or Cr layer are very noise and shown dotted; only positions with significant counts in both edges are marked by the solid line. Interestingly, the maximum B peak coincides in depth position roughly with where the lower row of bright patches in Fig. 6d occurs, suggesting that these are indeed due to small B-rich precipitates.

4. Summary

In summary, boron was detected by energy-filtered imaging in the form of sub-nanometre tiny platelets clustered around 4nm depth below the original wafer surface (now SiO$_2$/Cr interface). Energy-loss spectroscopy of the silicon and boron signals has yielded an effective B concentration in the SiO$_2$ of ~3 at% and in the Si of a maximum of 4 at%, which corresponds to the clusters observed. These values agree with the experimental shoulder observed in the SIMS profile at about 4nm sputter depth, but disagree with the B-rich spike reported by SIMS nearer the surface. No evidence for B concentrations above 5 at% was found, neither could we find extended lattice defects or precipitates.

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