The Effect of Oxidation and Carbon Contamination on SEM Dopant Contrast

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Abstract. Dopant contrast in the scanning electron microscope (SEM) has the potential to provide rapid and quantitative information about the distribution of dopant atoms in semiconductors providing that a robust quantification procedure can be developed. When silicon is exposed to air, it rapidly forms a native oxide on its surface which inevitably affects dopant contrast. In this paper we compare the dopant contrast observed on an in-situ cleaved specimen and an air-cleaved specimen and further examine the influence of prolonged electron exposure on dopant contrast.

1. Introduction
Dopant contrast in the scanning electron microscope (SEM) has the potential to provide a rapid, high resolution and quantitative dopant profiling tool for the characterisation of semiconductor devices. Dopant contrast in the SEM has been known for many years [1] but only received increased attention after the widespread introduction of field emission gun SEMs (FEGSEM) which led to an increase in signal to noise ratio [2]. Even though it is widely agreed that there is an approximately linear relationship between contrast and doping level [3], the mechanism which leads to the dopant contrast is still debated [4].

Regardless of the mechanism for dopant contrast, the fact that the condition of the surface of the material can affect dopant contrast is undisputed. It has been reported that altering the scan rate of image collection (hence altering the electron dose) changes the dopant contrast [5] and that carbon contamination on the surface can even go so far as to reverse the dopant contrast [6]. Although it is clear that surface layers undoubtedly play a role in dopant contrast, its effects have not yet been quantified.

In this paper, the effect of natural oxidation and carbon contamination (produced by cleaving in air) on dopant contrast is examined, as well as the effect of surface layer build-up by prolonged electron beam exposure such as in repetitive scanning of a p-n junction.

2. Experimental
A 3.3 µm thick p-type (boron doped: $5 \times 10^{18}$ atoms cm$^{-3}$) silicon layer was grown on an n-type (arsenic doped: $1 \times 10^{19}$ atoms cm$^{-3}$) silicon substrate using chemical vapour deposition (CVD). In order to collect Auger spectra, part of the wafer was cleaved in air and placed into vacuum with a time between cleaving and insertion into the specimen chamber of less than 3 minutes. The Auger electron spectrometer (AES) used was a Thermo Microlab 350. Auger electron (AE) spectra were collected...
using a primary beam accelerating voltage of 10 kV, an energy step size of 1 eV and a dwell time of 100 mS per energy step. For in-situ cleaving experiments, an additional piece of the wafer was clamped into a cross-section specimen holder and scored using a diamond scribe part-way across its width. The specimen holder was then inserted into the pre-vacuum chamber (pressure: $6 \times 10^{-6}$ Pa) and cleaved using a specimen manipulator. For in-situ cleaving, the investigated surface was not exposed to ambient air at any point.

To assess the thickness of surface layers formed by electron beam exposure, atomic force microscope (AFM) measurements were carried out using a Nanoscope III instrument with a tapping mode tip (330 kHz). For these experiments, a part of the silicon wafer was cleaved as previously described, before insertion into the vacuum chamber of the SEM again within 3 minutes of cleaving. Exposure was carried out in an FEI Sirion FEGSEM operating at an accelerating voltage of 1 kV, beam current of 78.5 pA and a working distance of 5 mm. A single scan consisted of scanning an area measuring 6 µm x 4 µm in a time of 3.25 s (a single scan delivers an electron dose of ~1.1 mC.cm$^{-2}$). The electron beam exposed silicon was examined using the AFM.

3. Results and Discussion

Figure 1 shows the result of imaging an ex-situ cleaved (in ambient air with ~3 minutes exposure) and an in-situ cleaved (cleaved under $6 \times 10^{-6}$ Pa vacuum) silicon test structure within the AES. The measured contrast (defined as the difference in intensity between p and n-type silicon divided by the average intensity) gives values of ~5% and ~10% for the ex-situ and in-situ cleaved silicon respectively. The AE spectra presented in figure 1 c give an explanation for this difference in dopant contrast. For ex-situ cleaving, the spectra exhibit peaks at ~265 eV and ~510 eV, which correspond to elemental carbon and oxygen respectively. There is no indication of the presence of these peaks in spectra obtained from the in-situ cleaved specimen indicating that the surface is less contaminated than the ex-situ cleaved specimen.

![Figure 1](image-url)

**Figure 1.** Secondary electron image of a silicon p-n junction cleaved (a) in-situ and (b) ex-situ and (c) Auger electron spectra showing the contamination present on p and n-type silicon after cleaving both in-situ and ex-situ with inset expansion of 80 – 100 eV.
It is remarkable that a surface layer adsorbed after only 3 minutes of exposure to ambient air, alters the dopant contrast, reducing it to half of that observed on an in-situ cleaved surface. A mechanism for this reduction was suggested as result of variation in oxide layer thickness in n-and p-doped regions [7,8] but there is no clear evidence for this in the ex-situ cleave AE spectra in figure 1 c, as there is no major difference in the oxygen peaks for p and n-doped regions respectively. Closer examination of the in-situ spectra between 30 eV and 100 eV, in particular the oxygen peak at 90 - 95 eV (figure 1 c inset) reveals that in-situ cleaved n-type silicon has a reduced peak intensity when compared to the in-situ cleaved p-type silicon. According to [9] this result suggests that a thicker natural surface layer has formed on the n-type silicon obscuring some signal from the underlying silicon, even after in-situ cleaving in a relatively high vacuum. In the ex-situ cleave, the 91 eV peak shows no consistent differences between n and p regions for the obtained data set (6 spectra).

As well as consideration of the formation of surface layers as a result of cleaving, it is also necessary to consider the dynamic effects of contamination caused by the deposition of contaminants by the scanning electron beam in an SEM, since dopant contrast has been found to strongly depend on electron dose [6].

![Figure 2](image_url)

**Figure 2.** (a) Atomic force microscope image of contamination present on silicon after 180 scans (area ABCD) with a 1 kV, 78.5 pA electron beam (221 mC.cm$^{-2}$) (step height ~3 nm at the dashed marker) and SE dopant contrast images of a p-n junction after (b) 1 scan and (c) 180 scans.

Figure 2 a is an AFM image of the surface topography after extended exposure of an ex-situ cleaved surface to a 1 kV electron beam with a total of 180 single scans (overall electron dose: 221 mC.cm$^{-2}$) in SEM. Here it can be seen that the area exposed to the electron beam (ABCD) is raised, indicating that the electron beam has led to deposition of material from residual gases in the chamber. This effect is more pronounced at the perimeter of the scanned area than in the center. The effect of the build-up of this surface layer on dopant contrast is demonstrated in figure 2 b and c. Images collected after 1 scan (figure 2 b) and after prolonged exposure (figure 2 c) show a reduction in dopant contrast from 14 % to 5.5 %. Figure 3 shows the relationship between the number of SEM scans and the dopant contrast observed together with the approximate thickness of the SEM deposited contamination (as measured by AFM). The thickness measurements were taken from positions similar to that indicated on figure 2 a. The dopant contrast is reduced dramatically between 1 and 20 scans which corresponds to less than 1 nm of surface layer growth. A similar dramatic reduction in dopant contrast is also observed when preparing silicon surfaces using focused ion beam (FIB) for site-specific dopant contrast imaging, where a damaged layer measuring only 5 nm can cause a ~50 %
reduction in dopant contrast [10]. Both the results presented here and the result of FIB damage reported in [10] indicate the importance of the consideration of the condition of the silicon surface for the use of dopant contrast.

When examining ideal laboratory structures (as used in this study), dynamic build-up of surface layers with electron beam exposure has little impact as it is always possible to examine an adjacent unscanned area. However, when using real semiconductor devices, imaging a new area may not be an option. Therefore, this dynamic alteration of the surface during scanning adds an extra level of complexity to the challenge of accurate quantification of dopants using SEM, and must be included in any numerical calculations which attempt to quantify dopant contrast.

4. Conclusions
A surface layer which forms naturally on cleaving silicon in air has a significant effect on the dopant contrast. We observed a reduction in dopant contrast of 50 % when comparing ex-situ cleaved silicon to an in-situ cleaved sample (when imaged in an AES). In addition, dopant contrast can be even further reduced by the build-up of deposited surface layers as a result of electron beam exposure. In order for SE dopant contrast to be considered as a quantitative dopant mapping tool, the effects of the surface contamination must be taken into account.

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