The chemisorption of oxygen and its effect on the secondary electron emission from doped semiconductors

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Abstract. The determination of the dopant concentration in semiconductors at the nanometre scale is an important technological goal. One possible approach is to use the dopant contrast (DC) effect in low voltage scanning electron microscopy (LVSEM). The DC effect normally causes p-doped semconducting material to appear brighter than n-doped in a LVSEM and the contrast is dependent on the dopant concentration. In this report we have studied highly doped p- and n-type silicon with thick oxide layers and after the oxide layer was removed by dipping in diluted HF. DC was measured as a function of primary beam voltage. It was found that the DC could be reversed (i.e. n-type brighter than p-type) at higher primary beam voltages for the thicker oxide, but such reversals were not apparent for the thinner oxide. By comparing with results from different electron emission techniques such as photoemission and field emission it can be concluded that oxygen plays an important role in DC not just for monolayer thicknesses as previously recognised, but also for much thicker oxides.

1. Introduction

The discovery that differently doped regions of a semiconductor can produce differing levels of secondary electron (SE) emission in a scanning electron microscope (SEM) was first made by Chang and Nixon [1]. The contrast between the two regions is known to be dependent on the n-type dopant concentration [2]. The dopant contrast (DC) effect could be a useful tool for the semiconductor manufacture industry if it could be fully understood and quantified [3]. However, the root cause of the effect has been in dispute for a number of years. The most often quoted theory is the “Patch field” theory [4] which explains DC as being due to electrostatic fields external to the sample. Another theory attributes DC to the band bending near the surface caused by the native oxide [5] and another that there are differing inelastic mean free paths (IMFP) for the SEs in the differently doped semiconductors [6]. Chakk and Horvitz [7] suggested a dynamic charging mechanism. The York group have promoted yet another alternative theory suggesting that surface contamination – principally carbon – causes a surface energy barrier similar to that of a Schottky barrier [8-10]. Duraud et al. [11] proposed that oxygen played a role in the DC which was mainly due to varying thicknesses of the oxide layer but a deeper explanation was lacking.

In this paper we present data on the effect of the thickness of the oxide layer on the contrast as a function of the primary beam. We then discuss these results in the context of other reports using different electron emission techniques (such as field emission and photoemission).
2. Experiment

Boron patterns were diffused into a (111) silicon wafer (phosphorus-doped n-type silicon substrate) at a temperature of ~1000 K. The n-type substrate was doped to a level of ~\(10^{15}\) cm\(^{-3}\) while the p\(^+\) regions were doped at ~\(10^{19}\) cm\(^{-3}\) to a depth of ~3 \(\mu\)m.

The native oxide was thinned by ultrasonic cleaning in IPA followed by dipping in 10:1 H\(_2\)O:HF. An SEM (type Tescan, TS5136MM) was used to image the sample at a variety of beam energies. The SEM was equipped with an Everhart-Thornley (ET) detector for the acquisition of the SE signal. The equation to determine the DC, \(C_{A/B}\), between two differently doped areas A and B is given by:

\[ C_{A/B} = I_A - I_B \]  

where \(I_A\) and \(I_B\) are determined from the greyscale level of the image (white equals 1 and black equals 0). It was ensured that the sensitivity of the ET detector did not vary between the acquired images. The highly doped p\(^+\) type region is assigned to region A and the lightly doped n type areas is assigned to region B. In order to allow a substantial oxide layer to grow, the samples were stored in air at atmospheric pressure for several months prior to the experiments. The first set of SEM images were carried out on the oxidised samples. The samples were then subjected to the procedure described above to remove the oxide layer and then re-imaged in the SEM. The reader is directed to [12] for further details.

3. Results

Upon imaging the oxidised sample at a primary energy (PE) of 1 keV it was found that the p\(^+\) regions have a greater SE emission than the n regions as has been found many times before. However, a DC inversion was found at higher PE (see Figure 1).

![Figure 1. SE images of an oxidised Si (111) sample (a) 1keV and (b) 7keV. Image size: 1.04mm x 0.87mm.](image)

Upon removing the oxide, it was found that the DC continued to vary with PE, although no contrast reversal was found. Using equation (1), the DC was determined for a range of PEs for samples with and without the thick oxide layer. The results are shown in Figure 2. Sealy et al. [4] also studied DC as a function of PE, but they did not find DC reversal.
4. Discussion
The results shown above clearly indicate that thick oxide layers have a major influence on the DC effect. The cause for this could be due to charging within the surface oxide layer, although why the charging should influence the SE emission from one doped region more than another is unclear. In addition, the results shed little light on the current competing theories which attempt to explain DC.

4.1. Electron emission from semiconductors – a look at the literature
More insight into the DC mechanism can be obtained from papers using other electron emission techniques. These techniques include photoemission (PE) and field emission (FE).

4.1.1. Photoemission.
It is well known that the native oxide on Si can induce considerable surface band bending. Indeed, in a PE study undertaken by Wagner and Spicer [13] using in-situ cleaved doped Si surfaces it was revealed that the valence band maximum of n-type Si shifts to a ~0.4eV higher binding energy upon exposing the surface to a single monolayer of oxygen. This fact has consequences for the foundations of the “patch field” theory [4] as this theory assumes that the energy required to remove an electron from the semiconductor into the vacuum is independent of whether it is n-type or p-type (see Fig 8 of ref [4]). The results of Wagner and Spicer [13] call this assumption into question as it is not clear whether the argument proposed by Sealy et al. [4] is for the case where no oxygen is on the Si surface or when a layer of oxygen is deposited on the surface. Ballarotto et al. [14] used Photoelectron Emission Microscopy (PEEM) to study doped semiconductors and also used the presence of oxygen to explain their results. Their theory has very close similarities to that of Perovic et al. [5]. If significant external electrostatic fields were present, then one would expect the PEEM results of Ballarotto et al. [14] to appear distorted – they are not.

4.1.2. Field emission
Johnson et al. [15] studied FE from p- and n- doped Si whiskers as the extraction voltage was varied. It was found that there was a delayed onset to the FE from n-type Si. This suggests that there was an energy barrier that the electrons emitting from the n-type semiconductor had to overcome. It is difficult to imagine how an electrostatic field external to the sample could induce such an effect. In addition, such a delayed onset of the FE is not consistent with the hot electron IMFP theory [6].

4.2. Electronic effects due to chemisorption
Chemisorption on semiconductors is known to behave differently than on other materials, e.g. metals [16] and the theory describing how gases adsorb onto semiconductors underpins much of the gas
sensor technology available today. The adsorptivity is controlled according to whether the adsorbing gas is an “acceptor” (i.e. accepts an electron from the substrate) or a “donor” (i.e. donates an electron to the substrate) and the position of the Fermi level within the band gap (i.e. whether the substrate is n-type or p-type). From the predictions on absorptivity [16], one might expect the native oxide to be thicker on n-type than on p-type semiconductor. This seems to be borne out by experiment [17]. The deposition of different materials on the surface will have different effects on the band bending which has been discussed within the context of DC before [8-10].

4.3. The effect of a thicker oxide on the dopant contrast
Since the native oxide is an insulator, this could well influence the SE emission (especially for thicker oxides), as has been extensively discussed by Cazaux [18]. Contrast reversals due to variations in primary beam voltage, charging effects and scanning frequency were discussed. The possibility that the oxides had different thicknesses on the n- and p-type substrates may explain their different behaviours under the primary electron beam.

5. Conclusions
From the results presented here, the thickness of an oxide layer clearly influences the DC of heavily doped semiconductors. This may be due to charging effects on thick oxides. In addition, by considering results from the literature it is clear that oxygen plays a role in DC even for very thin oxide layers. Well understood chemisorption on semiconductor theory can explain the literature results for photoemission and field emission but cannot be used to explain the contrast reversal as a function of primary beam energy for thick oxides found here.

Nevertheless, it is important that, in future, all interpretations of DC results consider the presence of oxygen (and other contaminants) whether sub-monolayer or several microns in thickness.

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