Abstract— The way in which the plasma in the ion source interacts with the constituent elements of the source chamber can provide important insights into the plasma chemistry and may facilitate improvements in ion source design and operation. It is also an important parameter in determining the environmental impact of the implantation process. It is worth noting that less than 0.4% of the material placed into the ion source is actually implanted as a dopant into the target wafers; the rest remains as a solid residue or gaseous emission. As many of the materials used for dopant implantation are either highly toxic, pyrophoric, greenhouse gases or powerful ozone depleters, or combinations of the above it is imperative, that the extent, location and chemical composition of these residues are quantified and understood. This will enable their impact on the environment, economy and society, the three pillars of sustainable development [1] to be assessed. In this study small pieces of silicon were placed at pre-determined points within the source chamber of a commercial ion implantation system. Antimony was then run using SbF3 as the feed gas. At the end of the run the silicon samples were retrieved and analysed using Rutherford Backscattering (RBS) and ion channelling. It was found that the location of the samples influenced the elemental composition of the plasma products deposited in the source chamber. A similar experiment was also conducted for BF2+ implants using a BF3 feed gas, again the elemental composition varied with the position of the silicon samples allowing the distribution of different elements, within the plasma products, to be mapped around the source chamber.

Ion implantation, plasma products, implant residues, plasma-dopant interactions, Rutherford Backscattering (RBS), Sb implantation, B implantation, silicon.

I. INTRODUCTION

The rapid expansion of the semiconductor industry has necessitated the use of advanced but often environmentally intensive manufacturing technologies. Given the rate of growth of this industrial sector, it is now imperative that further technological developments are designed and engineered so as to satisfy the principles and criteria of sustainable development [1-2].

From an environmental approach, there are several concerns associated with ion implantation and they lie in the choice of doping materials and operation of the ion implanter.

The principal compounds used as source feed materials in silicon technology are; BF3, AsH3, PH3, SbF3 and SiH4. Many of these materials are either highly pyrophoric or highly toxic or both, the fluorides are also powerful ozone depleters and all of them are greenhouse gases. The size of the industry, and the negligible amount of dopant (0.4%) that is actually implanted in the target wafer, means that relatively large quantities of highly toxic and polluting waste materials need to be treated and disposed of. The main issue, however, is not the quantity of the materials but the toxic effects of the wastes which are disproportionately larger than the quantities alone would suggest.

There is a dearth of literature in this area, Amo et al [3] and Hayes et al. [4] have studied exhaust emissions during ion source operation and during vacuum pump regeneration. Larson et al. [5] have suggested that liquid species such as tertiarybutylarsine (TBA) and tertiarybutylphosphine (TBP) are less toxic than their gaseous counterparts (AsH3 and PH3). However, the use of TBA and TBP leads to carbon deposition in the source and compromises its ionisation efficiency. The use of TBA and TBP also leads to the emission of hydrocarbons which are highly undesirable environmentally, being the precursors of photochemical smog.

The work reported in this paper seeks to identify where in the source chamber the waste residues accumulate and how they are affected by the source operating conditions. This research will probe the plasma chemistry within the ion source and should thereby facilitate improvements in ion source design and operation. The results will subsequently be used to inform and direct the life cycle analysis (LCA) of ion implantation systems, allowing more sustainable, environmentally friendly systems to be developed.

II. EXPERIMENTAL

Small silicon samples (1cm²) were inserted into the source chamber, beneath the source. Two samples (Sb1 and Sb2) were inserted above the cool tube, where the source is inserted (Fig. 1). The cool tube is located above the source bushing, which is used to insulate the source from ground. Another four samples (Sb3-6) were inserted beneath the cool tube in
the source bushing (Fig.2). Sb was then run for 8 hours using an indirectly heated cathode (IHC) source with SbF₃ as the feed material. Subsequent to Sb implantation the source was vented and the silicon samples removed. A reference sample was also prepared, this was not placed in the source chamber but was otherwise treated identically. A second set of samples was also prepared, again, with a suitable reference sample. This time the feed gas was BF₃, the implanted species BF₂⁺, and the samples placed in positions 3, 4 and 5 in Fig.2. This time the implanter was run for much longer (60 hours).

For all samples random and channelled Rutherford Backscattering Spectrometry (RBS) measurements, were undertaken using 1.5 MeV He⁺ ions at normal incidence with two detectors mounted at scattering angles of 163° (detector A) and 133° (detector B). Ion channelling was facilitated by the use of a 2 axis goniometer, which also allowed the sample to be rocked during the collection of the random spectrum, ensuring that a true non-aligned spectrum was obtained. The RBS data (from the random spectra) were fitted with the IBA Data Furnace [6]. The random spectra are insensitive to light elements: the signal to noise ratio is improved by channelling and the light elements quantified from their respective signal areas. Areal concentrations are given throughout this paper since these do not require the density of the deposited layer to be known and can be calculated directly from the RBS results.

III. RESULTS & DISCUSSION

3.1 Plasma Products produced during Sb Implantation

Fig. 3 shows the random and channelled RBS spectra for the silicon sample taken from position 1 (Fig. 1) after Sb had been run for 8 hours. For reasons of clarity only the spectra from detector A are shown. The major impurities found on the silicon surface are shown by arrows in Fig.3 and identified as W, Sb, Mo, As, Fe, F, O and C. The concentrations for each of these elements in sample Sb1 are shown in Table 1. For the reference silicon sample no impurities were detected by RBS.

![Figure 3 Random & channelled RBS spectra for Sb1](image)

### Table 1. Samples Sb1-6 Elemental impurities in plasma products

<table>
<thead>
<tr>
<th>Sample</th>
<th>W</th>
<th>Sb</th>
<th>Mo</th>
<th>As</th>
<th>Fe</th>
<th>F</th>
<th>O</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb1</td>
<td>4.8</td>
<td>5.6</td>
<td>2.5</td>
<td>9.1</td>
<td>47</td>
<td>30</td>
<td>18</td>
<td>78</td>
</tr>
<tr>
<td>Sb2</td>
<td>0.88</td>
<td>3.1</td>
<td>0.23</td>
<td>1.2</td>
<td>47</td>
<td>30</td>
<td>18</td>
<td>78</td>
</tr>
<tr>
<td>Sb3</td>
<td>0.33</td>
<td>0.32</td>
<td>0.095</td>
<td>0.21</td>
<td>0.45</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb4</td>
<td>0.43</td>
<td>0.53</td>
<td>0.086</td>
<td>0.042</td>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb5</td>
<td>0.33</td>
<td>0.43</td>
<td>0.43</td>
<td>0.21</td>
<td>0.34</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb6</td>
<td>0.47</td>
<td>0.78</td>
<td>0.11</td>
<td>0.76</td>
<td>0.45</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig 4 compares the results from the samples placed at positions 2-6 (Sb2-6). The concentrations of F, O and C in these samples were below the RBS detection limits. The elemental concentrations for these samples can also be found in Table 1.

From the RBS it is clear that the highest areal concentrations of impurities (i.e. the thickest deposits) are found on samples Sb1 and Sb2. These are the two samples placed above the cool tube. Sample Sb1 shows the highest areal concentration of elemental impurities. This is not really surprising since sample Sb1 is located beneath the arc chamber, where the plasma was generated and so might be expected to have the highest concentration of plasma products on its surface. Sample Sb2 was more remote from the arc chamber.
chamber but still shows appreciable areal concentrations of plasma products. Samples 3-6 were located beneath the cool tube in the source bushing with one sample in each of the ripples in the bushing, with 3 being closest to the source and 6 being furthest from it. The areal concentrations of impurities for samples Sb3 to Sb6 are essentially very similar, however, sample Sb6 shows slightly higher levels of As and Sb.

The presence of Sb in samples Sb1-6, is explained by the fact that the predominant ion species in the plasma are Sb$^+$ and SbF$_2^+$ (this also explains the presence of F in sample Sb1). The Fe in the samples is thought to come from the heating of the stainless steel in the solid source assembly. As most of the ion implanter is, however, made from stainless steel it is possible that some of the Fe comes from other sources. Although As was not implanted in this experiment it had been implanted previously on the ion implanter. Arsenic is known to have a long residence time and resides in the graphite and tungsten liners. As these become hot the resident As becomes more mobile as evidenced by the fact that the areal concentrations of As and Sb are similar, in samples Sb3-6, even though Sb is the species being implanted. The Mo is thought to originate from the sputtering of either the cathode and or the retaining clamps in the arc chamber. Some Mo may also come from the extraction electrode screws or trace quantities of Mo in the W liners. The W found in samples Sb1-6 is likely to come from sputtering and or reactive ion etching of the W anode, cathode and liners in the arc chamber. It is thought that the oxygen detected in sample Sb1 is in the form of an oxide, probably SiO$_2$, formed when the source chamber was vented. The oxidation may have been enhanced by the presence of W in the surface layer, which is known to enhance the rate of oxidation. The higher concentrations of W in sample Sb1 may account for the fact that O is only observed in this sample.

### 3.2. Plasma Products produced during B Implantation

Fig 5 shows the channelled RBS spectrum taken from the silicon sample placed at position 5, while BF$_2$ was implanted over a period of 60 hours (sample B5). RBS spectra taken from the reference sample showed no detectable impurities, whereas those taken from sample B5 showed C, O, F, Mo and W impurities.

Figure 6 plots the areal concentrations of W, F, O and C for each sample i.e. those taken from positions 3, 4 and 5 in Fig. 2 (samples B3, B4 and B5 respectively). The results for all the impurities are tabulated in Table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>W</th>
<th>Mo</th>
<th>O</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3</td>
<td>17</td>
<td>27</td>
<td>60</td>
<td>25</td>
</tr>
<tr>
<td>B4</td>
<td>19</td>
<td>35</td>
<td>0.56</td>
<td>26</td>
</tr>
<tr>
<td>B5</td>
<td>12</td>
<td>0.52</td>
<td>28</td>
<td>0.44</td>
</tr>
</tbody>
</table>

The implant time for BF$_2$ was almost ten times that for Sb$^+$ (60 hours as opposed to 8) therefore it is not surprising that the areal elemental concentrations are higher for the former set of samples than the analogous set for the latter. The W observed in the samples B3-B5 is thought to come from the arc chamber liners and the anode and cathode. The Mo observed in sample B5 could be due to Mo impurities in the W liners. Like the Sb implanted samples the O in samples B3-B5 is thought to be in the form of an oxide, the growth of which is enhanced, at the time when the source is vented, by the presence of W in the deposit. The C in samples B3-B5 is thought to be caused by the erosion of the source electrodes by the ion beam. The F comes from the source gas BF$_3$. Interestingly no As, Fe were detected in this set of samples unlike the earlier set with Sb. It should be noted that a gaseous source was used for BF$_3$, whereas for Sb, a solid source of SbF$_3$ was employed. The lack of Fe in the former set of samples seems to reflect this difference in source assembly.
Samples B3-B5 were placed below the cool tube in the source bushing which is made of insulating ceramics. All of the samples show areal concentrations of W in excess of $1 \times 10^{16}$ atoms cm$^{-2}$. A build up of W on the source bushing ceramics could create premature tracking and is an area that requires further study.

When fluorinated species are used as the source gas the extreme reactivity of fluorine is known to have a deleterious effect on the source and the liners of the arc chamber, leading to the formation of residual deposits (flakes) in the source chamber [7]. It is likely that the thickness of the plasma deposits observed in this study on samples Sb1-6 and B3-5 are a consequence of F enhanced sputtering and reactive ion etching. The fact that fluorinated species can directly or indirectly compromise the performance of the source coupled with their adverse effect on the environment suggests that alternative feed gases are highly desirable and may be essential in Europe when legislation [2] outlawing the use of halogenated species and their pre-cursors reaches the statute books.

IV. CONCLUSIONS

For the samples Sb1-6, where SbF$_3$ was run as the source gas (for 8 hours) to generate a Sb$^+$ beam, the silicon samples placed above the cool tube (Sb1-2) were found to have higher areal concentrations of W, Sb, As, Mo, Fe, F, O and C than those placed below the cool tube (Sb3-6). Sample Sb1 located beneath the arc chamber had the highest concentrations. The W in the deposits is thought to result from the sputtering and or reactive ion etching the arc chamber liners, anode and cathode. Likewise C is thought to be generated by the action of the ion beam on the extraction electrodes. The presence of Fe appears to come from the heating of the stainless steel in the solid source assembly. The presence of As is a memory effect caused by this species having been previously implanted and is facilitated by the long residence time of As in the liners of the source. The smaller amounts of Mo are thought to come from clamps and screws within the source assembly and or from Mo impurities in the W liners.

For the second set of samples where BF$_3$ is run for 60 hours significant quantities of F, C, O and W were detected in the deposits. The origins of the W and C are similar to those for SbF$_3$. The F comes from the feed gas and it is thought that the O is in the form of an oxide, which is formed when the source chamber is vented. The growth rate of this oxide is likely be enhanced by the presence of W. The presence of W on the source bushing may produce premature tracking and lead to a breakdown in insulation. This work illustrates that insights can be obtained into the plasma chemistry that pertains during ion source operation by analysing the waste residues within the source chamber. These results will be used to inform Life Cycle Analysis and environmental impact studies on this stage of semiconductor processing.

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[1] United Nations Resolution 44/228


