The local structural characterization of the inactive clusters in B, BF$_2$ and BF$_3$ implanted Si wafers using X-ray techniques

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Abstract

Characterization of the inactive clusters formed by high dose implantation silicon are one of the crucial topics in the semiconductor industry. Analytical techniques, which could provide quantitative information on the detailed description of the complexes that are formed at dopant concentrations above solid solubility levels, are valuable to post-implantation researchers. Previously, X-ray absorption fine-structure spectroscopy (XAFS) studies of the As and Sb implanted Si wafers revealed not only that of the chemical nature of clusters, but also the arsenic case, the ratio of the precipitated versus the substitutional form of the As in the system [1,2]. In this study, we have used F K-edge and Ge K-edge (for the Ge pre-amorphized wafers) XAFS in order to probe the nature and of the clusters in B, BF$_2$ and BF$_3$ implanted Si wafers. Implants with various doses and implant energies were subjected to various annealing techniques such as laser annealing, spike annealing, solid state phase epitaxy, and flash annealing and the evolution of the spectral features of the clusters were followed upon annealing. The theoretical multiple scattering XAFS calculations were performed in order to correlate the spectral features in the XAFS data with the near-neighbor configuration around the main absorbing atom. The identification and the relative weight of the clusters after different annealing conditions will be presented in order to provide insight to the optimum annealing conditions in these systems.

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1. Introduction

In order to sustain the same electrical conductivity in ever shrinking doped regions of Si-based semiconductor devices doping with B is essential. However, the conductivity can only be increased by heavy B doping up to a certain level since high dose B doping starts to form electrically inactive clusters instead of simply substituting Si atoms in the crystal.

Various thermal annealing techniques such as rapid thermal processing (RTP), laser annealing (LA), solid state phase epitaxy (SPE) are being investigated for application after high dose boron ion implantation in order to reduce the B clustering in Si. In these attempts of finding the best post-implantation treatment to reduce the clustering, the local structural information around the impurity and the Si atom plays a crucial role. Therefore, local structural probes such as XAFS are very useful in providing the near-neighbor distribution around the impurity atom. XAFS being an element specific method can be selectively used for studying the local structure around a specific atom in the material. Furthermore, the structures to be studied by XAFS do not need to exhibit a long-range order. The Fourier Transformed (FT) XAFS data contains information on the near-neighbor distances and the coordination numbers around the selected absorbing atom. As shown previously, using theoretical XAFS scattering models in conjunction with the FT data provides important information on the nature of the formed clusters or precipitates in various Si dopants [1–6].

In this study, Ge pre-amorphized ultra low energy (ULE) B, BF$_2$, and BF$_3$ implanted Si wafers were used to probe the local structural modifications caused by high B concentrations in the Si crystal. Since the Ge K-edge has a very
distinctive XAFS signal, which is extremely sensitive to local structural modifications, we have selected the Ge atom as the main absorbing atom in the first part of this work. We have used University of Washington’s multiple scattering XAFS calculation code FEFF7.0 [7] in order to calculate scattering contributions from all possible local structures around the Ge atom for B and BF₂ implants. Using the XAFS amplitudes and phases from FEFF7.0 calculations in the non-linear least squares XAFS fits the effects of the different implant species and thermal annealing processes on the formation of clusters were revealed. The samples used in this study were 250 eV B and 1.1 keV BF₂ as-implanted, laser annealed (LA) and rapid thermal processed (RTP) samples. The B concentrations in the region of interest for these samples were well above the solid solubility limit of B in Si. The emergence of a shoulder peak and non-linear least squares fit results to the FT data of the B and BF₂ implanted Si indicate clearly the presence of Ge–B clusters in the BF₂ implanted RTP samples. The F K-edge results on the BF₁ implanted Si exhibits the effects of the SPE and RTP in dissolving the F involving clusters in the form of F–Si, F–B.

2. Experiment

Si(100) wafers were pre-amorphized with 30 keV, 1×10¹⁵ atoms/cm² Ge implants. The wafers were then implanted with 250 eV B⁺ and 1.1 keV BF₂⁺ ions, respectively, at a dose of 1.0×10¹⁵ atoms/cm². After the implantation, the wafers were subjected to laser annealing, and rapid thermal processing (RTP). For laser annealing a 308 nm Excimer laser was used with an exposure for 20 ns at a laser fluence of 0.62 J/cm². The RTP conditions were at 1050 °C for 1.4 s duration at the peak temperature in N₂ ambient. The implantation energy and the dose for the BF₁ in Si samples were at 600 eV and 2×10¹⁵ atoms/cm², respectively. BF₁ implanted samples were subjected to solid-state phase epitaxy and RTP after the implantation. Germanium K-edge X-ray absorption fine structure spectroscopy (XAFS) experiments were performed at the National Institute of Standards and Technology’s (NIST) beamline (X23A2) at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory (BNL) using fluorescence detection mode with the X-ray angle of incidence set approximately twice the Si critical angle during the measurements. F K-edge XAFS data were acquired in the total electron yield mode at the Beamline U1A of NSLS.

3. Results and discussion

In XAFS data analysis, the energy dependent absorption coefficient was normalized to the absorption edge after the atomic absorption was subtracted [8]. The Fourier transformation of the resulting XAFS function, χ(k), provides the pseudo-radial distribution around the main absorbing Ge atom. The Fourier Transformed (FT) data obtained from the XAFS function using a Gaussian window for the (2.5–11.0 Å⁻¹) k-range for the Ge K-edge. The peaks appearing in the FT data are due to back scattering from the near-neighbors of the main absorbing Ge atom and the positions and intensities are related to near-neighbor distances and coordination numbers of the surrounding atoms. The peak distances are shifted from the actual near-neighbor distances because of the additional phase shift due to back scattering from the surrounding atoms.

Fig. 1 shows the FT data for the 1.1 keV 1.0×10¹⁵ cm² BF₂ implants with the non-linear least squares XAFS fit (dotted line) to the data. The dashed-line is the multiple scattering simulations for the second shell using only Ge–Si multiple scattering contributions. The fit (dotted line) on the other hand involves scattering contributions from Ge–B clusters too. It is easily noticeable that a shoulder appears in the FT peak of the second shell. This shoulder peak would not be present if the implant were only Ge in Si, where the Ge atoms replaced some of the Si crystal sites. The simulation results using only Ge–Si scattering confirm this as shown in the plot with the dashed line. The shoulder peak can only be reproduced by including the scattering paths involving the clusters of atoms of Ge and B. The scattering paths for the non-linear least squares fit shown in the plot as the dotted line were created using clusters including B, F, Si and Ge atoms, however, the Ge–B scattering is the only major contributing component to the shoulder peak.

Fig. 2 is a plot of the FT data for the as-implanted, laser annealed, and RTP BF₂ in Si samples. The first and second-shell peaks are labeled according to the contributing
scattering paths to the resolved peaks. The second-shell peak for the as-implanted sample is much weaker compared to the annealed samples indicating the damage to the crystal structure after implantation and lack of long-range order beyond the first shell due to implantation induced amorphous structure. Although the Ge–B shoulder peak is present at the same location in the laser annealed sample, it is not as pronounced as the RTP sample. The least square fits to the second shell for the laser annealed and the RTP samples are also plotted as dotted lines. As in the case of the RTP samples, the fits to the LA samples are performed including the Ge–B scattering. The fits are in very good agreement with the data only when the Ge–B scattering is included in the FEFF 7.0 created theoretical standards for the local structure. Laser annealing formed a complete melt in the crystal for a short period that leads to better recrystallization at the end of the annealing process. Laser annealing has been shown to be effective in repairing the damage to the crystal due to implantation and recovering the active carrier concentration in many systems [3,9]. This provides a possible explanation for the rather weak Ge–B peak in the FT data of the LA samples. It appears that LA is dissolving the Ge–B clusters, which were evidently present after rapid thermal processing on these BF2 implants. The Ge–B shoulder peak in the FT data appears at a shorter distance than the Ge–Si scattering peaks. These spatial differences between these two peaks actually enable us to differentiate between the Ge–B and Ge–Si scattering. Otherwise the larger amplitude of the Ge–Si scattering would dominate making the Ge–B scattering negligible in the second shell.

The FT data for the as-implanted, laser annealed, and RTP B samples are shown in Fig. 3. For the B implanted samples the Ge–B peak is still present, but less intense compared with the BF2 implanted samples. Here again the as-implanted sample indicates an amorphous structure. The differences in the Ge–B peaks are subtle in comparison, between the LA and the RTP samples for the B implants, though the RTP sample seems to have slightly higher intensity for this shoulder peak. The least square fits (dotted lines), in which Ge–B and scattering contribution is still present, but minimal compared the BF2 implants are in agreement with the FT data.

Fig. 2. Fourier Transformed (FT) Ge K-edge XAFS data for the as-implanted, laser annealed (LA), and rapid thermal processed (RTP), Ge pre-amorphized 1.1 keV BF2 implants in Si. The scattering contributions to individual peaks are noted on the plot. The dotted line is the least squares XAFS fit to the second-shell using theoretical (FEFF7.0) standards including Ge–B–Si local structures.

Fig. 3. Fourier Transformed (FT) Ge K-edge XAFS data for the as-implanted, LA, and RTP, Ge pre-amorphized 250 eV B implants in Si. The scattering contributions to individual peaks are noted on the plot. The dotted line is the least squares XAFS fit to the second-shell using theoretical (FEFF7.0) standards including Ge–B–Si local structures.

Fig. 4. Overlay of RTP samples.
Figs. 4 and 5 are the overlay plots of the laser annealed and RTP samples for a direct comparison of the second-shell peaks mainly the Ge–B shoulder. Qualitatively, the peak has the highest intensity for the RTP BF2 implanted sample. If the annealing method is the same then, the BF2 implants show a more robust peak than the B implants. The non-linear least squares fit results for the B and BF2 implanted samples are listed in Table 1. The coordination number ($N_{\text{Ge–B}}$) for the Ge–B scattering for BF2 implanted RTP sample is singled out from the rest of the samples as seen from the first column in the table. Similarly the coordination number for the Ge–Si scattering ($N_{\text{Ge–Si}}$) is significantly lower than the rest of the samples. The $N_{\text{Ge–B}}$ values show the trend as expected from qualitative observations inferred from Figs. 2–5 above between the B and BF2 samples and between the LA and RTP samples. Here the coordination numbers should be taken as a measure of the strength Ge–B contribution to the scattering rather than the exact structural configuration around the Ge atom.

In this description, for the RTP BF2 sample the presence of the Ge–B clusters is evident beyond the uncertainties of the fit results. The near-neighbor distance for the Ge–B clusters for the second shell is about 20% less than the second-shell Ge–Si separation. The laser annealed samples show relatively higher $N_{\text{Ge–Si}}$ values confirming better recrystallization and reduction in Ge–B clustering.

Fig. 6 is an overlay plot of the F K-edge XAFS data for the BF3 implanted samples. The absorption versus X-ray energy is plotted for the as-implanted, SPE and the RTP samples. The absorption data has been normalized above the F edge after a linear background subtraction determined by a pre-edge linear fit. The systematic decrease in the main F absorption feature in the direction of as-implanted, SPE and RTP indicate decrease in the F related clusters in the system. For the identification of the individual features further detailed XAFS scattering modeling will be performed at this energy range.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$N$</th>
<th>$R$ (Å)</th>
<th>$N$</th>
<th>$R$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF2 (RTP)</td>
<td>6.6 ± 0.5</td>
<td>3.06 ± 0.04</td>
<td>5.2 ± 0.5</td>
<td>3.81 ± 0.04</td>
</tr>
<tr>
<td>B (RTP)</td>
<td>3.6 ± 0.5</td>
<td>3.08 ± 0.04</td>
<td>7.9 ± 0.5</td>
<td>3.79 ± 0.04</td>
</tr>
<tr>
<td>BF2 (LA)</td>
<td>3.2 ± 0.5</td>
<td>3.09 ± 0.04</td>
<td>8.1 ± 0.5</td>
<td>3.80 ± 0.04</td>
</tr>
<tr>
<td>B (LA)</td>
<td>3.1 ± 0.5</td>
<td>3.10 ± 0.04</td>
<td>8.8 ± 0.5</td>
<td>3.80 ± 0.04</td>
</tr>
</tbody>
</table>

### 4. Conclusions and future work

Using Ge K-edge XAFS, the local structural differences around the Ge atom were probed for germanium pre-amorphized B and BF2 implants in Si. The wafers used were laser annealed and RTP annealed before being used in the XAFS studies. The goal was to probe the possible Ge induced clusters in these wafers to determine the structural differences in these structures under LA and RTP conditions. Ge K-edge XAFS results clearly indicate the emergence of a new shoulder peak in the second shell. Using the theoretical standards obtained by FEFF 7.0 multiple scattering XAFS code for all the possible local structural configurations, this new shoulder was identified as the scattering due to Ge–B clusters in the system. The non-linear least squares fit results to the second shell quantitatively confirm the increased strength for this Ge–B
scattering for the BF₂ implanted RTP samples. The results also indicate that laser annealing processes prevented the formation of these Ge–B clusters for both the B and the BF₂ implanted samples. The F K-edge absorption results indicate a decrease in the F related clusters in BF₃ implanted samples for the SPE and RTP samples, RTP exhibiting the least F clustering. In our future work, XAFS scattering modeling at the F K-edge will provide detailed information on the nature of the F clusters.

References


