IDENTIFICATION OF THE CARBON ASSOCIATED RADIATION DAMAGE LEVELS IN SILICON

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The dominant carbon related radiation damage centre in silicon was studied in detail. In contrast to previous studies the presence of two clearly distinguishable defects were established: one at $E_{C}+E_{T} = 0.370$ eV, $\sigma_p = 8 \times 10^{-18}$ cm$^2$ and assigned as the $C_8$–Si$_1$–C$_9$ complex, and another one at $E_{C}+E_{T} = 0.344$ eV, $\sigma_p = 1.1 \times 10^{-16}$ cm$^2$ and assigned as the COV$_2$ complex. It is suggested that the concentration of the $C_8$–Si$_1$–C$_9$ centre is indicative to the overall carbon concentration, hence the peak separation technique presented in this paper can be used to measure low - with IR absorption non-detectable - carbon concentrations in silicon.

INTRODUCTION

The yield and properties of very large scale integration (VLSI) devices which are mainly fabricated on Czochralski (CZ) silicon wafers are significantly influenced by the behaviour of oxygen in the silicon substrates. It is well established [1,2] that the presence of carbon in the silicon lattice significantly influences the precipitation properties of oxygen acting as a nucleation site. It is argued [1] that low carbon concentration is favourable. The widely used IR absorption technique can not usually detect carbon concentrations below $1 \times 10^{16}$ cm$^{-3}$ on samples with standard wafer thickness. Alternative ways to detect low carbon concentrations would therefore be welcome.

Radiation damage levels are the best characterized defects in silicon, only a selection of the published results are referenced here [3–9]. It was shown that the most common defects introduced by irradiation are complexes involving carbon and oxygen beside the simple point defects. In the present work we intend to concentrate on a carbon related level usually reported with $E_{C}+E_{T} = 0.36$ eV, which forms around room temperature and anneals out around 400 °C. This defect was first described more than 20 years ago [10] but its identity is still subject to controversy, the candidates being; COV$_2$ or C$_4$-C$_9$ (recently corrected as $C_8$–Si$_1$–C$_9$ by [11]). The intention of the present paper is to resolve this long standing controversy and suggest a calibration procedure for determining the concentration of carbon in silicon using the properties of
this defect.

EXPERIMENTAL

10-15 ohm cm 8 doped p-type silicon materials were used. Three groups of samples were selected:

<table>
<thead>
<tr>
<th>N&lt;sub&gt;D1&lt;/sub&gt; [cm&lt;sup&gt;-3&lt;/sup&gt;]</th>
<th>Float Zone (FZ)</th>
<th>Czochralski low C</th>
<th>Czochralski high C</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;10&lt;sup&gt;16&lt;/sup&gt;</td>
<td>5x10&lt;sup&gt;17&lt;/sup&gt;</td>
<td>5x10&lt;sup&gt;17&lt;/sup&gt;</td>
<td></td>
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<tr>
<td>N&lt;sub&gt;C1&lt;/sub&gt; [cm&lt;sup&gt;-3&lt;/sup&gt;]</td>
<td>&lt;10&lt;sup&gt;16&lt;/sup&gt;</td>
<td>&lt;10&lt;sup&gt;16&lt;/sup&gt;</td>
<td>5x10&lt;sup&gt;16&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Table I.

Schottky contacts were prepared by Ag<sup>+</sup> implantation (30 keV, 3x10<sup>16</sup> dose/cm<sup>2</sup>) as described in [12]. Subsequently the samples were implanted with H<sup>+</sup> at 300 keV and at room temperature, using varying dose levels between (4x10<sup>9</sup>-6x10<sup>10</sup>) dose/cm<sup>2</sup>. DLTS measurements were performed with a high sensitivity lock-in type spectrometer DLTS-82E, manufactured by Semitrap, Hungary.

RESULTS: DISCUSSION

Six radiation damage levels were observed in the majority carrier spectra, in the present work we concentrate only on the level, labelled as H<sub>4</sub> [13]. It was noted that the introduction rate of this defect is twice as high in CZ high C samples than that of the other levels. Detailed Isothermal Frequency-Scan [13] measurements were performed to determine the capture cross section of this level. Typical example is shown on Fig. 1. H<sub>4</sub> is produced as a recoil cascade process by the Ag<sup>+</sup> implant, the maximum is centered at 180 nm, and by H<sup>+</sup> implant centered at 2.7 μm. Capture cross section measurement on the proton induced defect was performed selecting the amplitude of the reduced reverse bias pulse to reach a defect free part of the junction in order to eliminate the influence of the free carrier tail on the capture rate. Two clearly distinguishable capture rates were measured. The values of the capture cross

![Figure 1/a](image)

Series of capture cross section measurements in frequency scan mode at T = 200 K

![Figure 1/b](image)

The corresponding evaluation of the two capture cross sections
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sections averaged over 8 samples (the accuracy of the individual measurements are better than 5%):

\[
\begin{align*}
\sigma_{\text{fast}} &= (1.1^{+0.1}_{-0.1}) \times 10^{-16} \text{ cm}^2 \\
\sigma_{\text{slow}} &= (8^{+2}_{-2}) \times 10^{-18} \text{ cm}^2
\end{align*}
\]

The much lower value reported by [6] for the slow process is probably due to the influence of the edge layer effect.

The \(H_4\) level induced by \(Ag^+\) implantation contains only the slow component, the \(H_4\) level induced by high dose \(H^+\) implantation in the \(CZ_{\text{lowC}}\) samples contains only the fast component within measurement accuracy. The peak labelled as \(H_3\) on Fig. 1/a, was not reported previously. This is mainly due to the superior energy resolution of the frequency scan technique. (To achieve equivalent energy resolution with temperature scan significant data points should be recorded at every 0.04 K). We believe that the large scatter - 0.33-0.38 eV - reported in the literature for the activation energy of \(H_4\) [2-9] is partly due to the admixture of \(H_3\). The capture cross section of \(H_3\) is \(\sigma_{\text{H}_3} = 2.7 \times 10^{-16} \text{ cm}^2\). It is important to decide whether the different capture rates observed for \(H_4\) originate from the same defect or we are dealing with two different species.

Using the Differential DLTS [14] variant of the Isothermal Frequency-Scan DLTS we succeeded to separate two levels. Two filling pulses, separated in time by half of the period lengths, with equal amplitude but different duration were used. The first pulse was long enough to fill both states, the second pulse filled only the faster state, hence the residual signal contained information only about the slower state. Alternatively, using a single filling pulse, short enough to fill only the faster state, the activation energy of the fast state can be determined independently. The result is illustrated on Fig. 2. The measured activation energies (averaged over 8 samples, the accuracy of the measurement on a single sample is \(\pm 1 \text{ meV}\)):

\[
\begin{align*}
(E_V+E_F)_{\text{fast}} &= (0.344^{+0.006}_{-0.006}) \text{ eV} \\
(E_V+E_F)_{\text{slow}} &= (0.370^{+0.002}_{-0.002}) \text{ eV}
\end{align*}
\]

For completeness, the activation energy for \(H_3\)

\[
(E_V+E_F)_{H_3} = 0.279 \text{ eV}
\]

The unusual accuracy of the measurement data (capture cross section and activation energy) is due to the thermal equilibrium conditions achieved during frequency scan. As a conclusion it can be stated that the peak separation technique described previously allows the determination of the individual concentration of the two components as well.

These types of measurements were performed on all proton induced \(H_4\) peaks in the three different kinds of materials as the function of proton dose. The dose dependence of the slow component of \(H_4\) is illustrated on Fig. 3. It is clearly seen that the relative weight of the slow component increases with increasing dose in the \(F_2\) and \(CZ_{\text{highC}}\) samples but decreases in the \(CZ_{\text{lowC}}\) samples. Based on these results we propose to identify the fast component with the \(COV_2\) complex [15] and the slow component with the \(C_{\text{Si}}=Si_{\text{C}}\) complex. Both defects form around room temperature via the mobile carbon interstitials [4]. It is assumed that the \(COV_2\) complex forms when \(C_{\text{i}}\) interacts with the already

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**Figure 2**

Arrhenius plots measured in frequency scan mode. The slow process was determined by the double pulse technique described in text.
present VO complexes. This reaction seems more favourable than the interaction with another carbon atom. The concentration of VO is, however, between \((10^{13}-10^{14})\) cm\(^{-3}\) in the samples investigated here while the carbon concentration is between \((10^{15}-5\times10^{16})\) cm\(^{-3}\), hence the formation of the CS-Si\(_I\)-CS complex becomes more preferable at higher doses. The only notable exception is the CZ\(_{lowC}\) sample at \(5\times10^{10}\) proton/cm\(^2\) where \(N_D/N_C-10^2\) as compared to other samples where \(N_D/N_C-10^4\), hence this data also supports our identification. Finally the \(H_4\) peak produced by recoil ions due to the \(3\times10^{16}\) Ag\(^+\)/cm\(^3\) implantation contains only the slow component. (The relative magnitude of the two components should be within two orders of magnitude to make it separable with the experimental technique used in the present work.) We assume that the \(H_4\) concentration measured near the M-S interface is the saturation value of CS-Si\(_I\)-CS:

\[
N_{H_4}^{[Ag^+]} = \begin{array}{ccc}
1\times10^{15} & 8\times10^{14} & 5\times10^{15} \\
\text{cm}^{-3} & \text{cm}^{-3} & \text{cm}^{-3}
\end{array}
\]

Table II.

From this assumption follows, that at intermediate doses

\[
N_{CS-Si_I-CS} = N_{sat}(1-e^{-x/a})
\]

or in linear approximation

\[
\frac{N_{CS-Si_I-CS}}{N_{sat}} = \frac{x}{a}
\]

where \(x\) is the proton dose/cm\(^2\).

To test the model the measured magnitudes of the slow components were plotted on Fig. 4, according to equation 2. The agreement seems to be satisfactory:

\[
a = 1.3\times10^{13}\text{ dose/cm}^2
\]

is determined from the model. Since two carbon atoms are needed to produce \(N_{H_4}\) the data in Table II suggest that about 20% of all carbon atoms present participate in creating CS-Si\(_I\)-CS at the saturation dose. Unfortunately the carbon concentration was measurable only in the C\(_{highC}\) samples, but our results do not contradict the IR absorption data for the other samples. (From the model \(N_C = 1\times10^{16}\) cm\(^{-3}\) in the FZ samples and \(N_C = 8\times10^{15}\) cm\(^{-3}\) for the CZ\(_{lowC}\) samples.)
CONCLUSIONS

It was shown that the dominant carbon related radiation damage level in silicon consists of two clearly separable components indentified as COV and C$_{Si}-$C$_{S}$ complexes.

The latter becomes the dominant defect at high doses and reaches a saturation value which is related to the overall carbon concentration in the sample. The experimental data support this model which on the other hand offers a simple procedure to determine the overall carbon concentration by measuring N$_{H_{4}}$slow at any given proton dose. To calibrate accurately the proposed carbon concentration measurement procedure large number of samples with different and known carbon and oxygen concentrations are needed. It would also be important to correlate the value of parameter a in equation 2 with the influence of annealing.

The proposed carbon concentration measurement procedure of this paper should be viewed as a next step on the way to use H$_{4}$ for determining oxygen and carbon concentration in silicon as originally suggested by Troxell [9]. On the other hand it is clearly established that the slow component of H$_{4}$ is the C$_{Si}-$C$_{S}$ complex which forms via the interaction of mobile carbon interstitials with substitutional carbon. It is suggested that the measurement of the lateral distribution of the C$_{Si}-$C$_{S}$ complexes by Scanning DLTS would reveal the oxygen precipitation around carbon atoms as nucleation sites.

ACKNOWLEDGEMENTS

We gratefully acknowledge to K.Schmalz the donating of the C$_{N}$ high samples, the extremely low dose implantation to H.Kerkow and the group of Prof.Klose and the IR data to F.Stallhofer and E.Hild. The stay of C.A.L. in Budapest was financed by the Greek-Hungarian Scientific-Technical Govermental Agreement.

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