Radiation Defects and Thermal Donors Introduced in Silicon by Hydrogen and Helium Implantation and Subsequent Annealing

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Abstract. The effect of high-energy hydrogen and helium implantation and subsequent annealing on generation of radiation defects and shallow donors in the low-doped oxygen-rich FZ n-type silicon was investigated. Samples were implanted with 7 MeV ⁴He²⁺ or 1.8 MeV ¹H⁺ to fluences ranging from 1x10⁹ to 3x10¹¹ cm⁻² and 1.4x10¹⁰ to 5x10¹² cm⁻², resp., and then isochronally annealed for 30 minutes in the temperature range up to 550°C. Results show that radiation damage produced by helium ions remarkably enhances formation of thermal donors (TDs) when annealing temperature exceeds 375°C, i.e. when the majority of vacancy-related recombination centers anneals out. The excess concentration of TDs is proportional to the helium fluence and peaks at 1.6x10¹⁴ cm⁻³ if annealing temperature reaches 475°C. Proton irradiation itself introduces hydrogen donors (HDs) which form a Gaussian peak at the proton end-of-range. Formation and annealing of shallow and deep hydrogen-related levels are strongly influenced by electric field at annealing temperatures below 175°C. If annealing temperature exceeds 350°C, HDs disappear and the excessive shallow doping is caused, as in the case of helium irradiation, by radiation enhanced TDs.

Introduction

Long range of light (hydrogen or helium) ions enables to locally modify electronic properties of silicon devices in their full depth. For this reason, the implantation of hydrogen or helium ions is widely exploited in silicon power device technology. Typical application is local reduction of carrier lifetime [1] or formation of ultra-deep n-doped layers [2]. The implantation is usually followed by low-temperature (<500°C) annealing which is used for stabilization/formation of produced radiation defects, mainly vacancy-related complexes. These defects interact with implanted hydrogen and intrinsic defects (interstitial oxygen) forming different shallow and deep levels in the silicon bandgap. These levels then significantly influence recombination/generation of excess carriers and doping profiles.

This paper systematically investigates effect of hydrogen and helium implantation and subsequent annealing on generation of radiation defects, hydrogen and thermal donors in the low doped FZ n-type silicon. The study is performed for implantation energies, fluences and annealing temperatures which are typically used for local lifetime reduction in power devices.

Experimental

Radiation defects and their influence on enhanced production of shallow donors was studied on the low-doped (phosphorus concentration below 10¹⁴ cm⁻³) <100>-oriented FZ n-type silicon substrate forming the n-base of the planar p⁺n⁻n⁺ diodes. Diodes had deep p⁺ and n⁻ emitters produced by long thermal diffusion which resulted in relatively high concentration of oxygen in samples. The diodes were irradiated from the anode side with 7 or 8 MeV helium ions in the range of fluences from 1x10⁹ to 3x10¹¹ cm⁻² and with 1.8 MeV protons at fluences ranging from 1.4x10¹⁰ to 5x10¹² cm⁻². The energies of helium and hydrogen ions (7 and 1.8 MeV resp.) were chosen to
guarantee an equivalent projected range of about 39.6 μm. After irradiation, the diodes were subjected to 30 minutes isochronal furnace annealing in the temperature range from 125 to 550°C. Proton irradiated diodes were also annealed at 125 and 150°C with applied forward and reverse bias to study effect of electric field on stability of shallow hydrogen donors and other hydrogen-related defects. Deep and shallow levels produced by irradiation and subsequent annealing were studied by the capacitance deep level transient spectroscopy (DLTS) using the DLS-82E and DLS-83D spectrometers and C-V profiling. The C-V measurement was performed by HP 4280 1 MHz capacitance meter at an elevated temperature (85°C) to minimize influence of deep acceptors connected with radiation damage on measured profiles of shallow donors [3].

**Fig. 1:** Evolution of the excess donors during annealing of the FZ silicon irradiated with 8 MeV alphas to a fluence of 1x10^9 cm^-2. Annealing temperatures 125 to 550°C, step 25°C – results of C-V measurement.

**Fig. 2:** Evolution of the excess donors during annealing of the FZ silicon irradiated with 8 MeV alphas to a fluence of 3x10^11 cm^-2. Annealing temperatures 125 to 550°C, step 25°C – results of C-V measurement.

**Fig. 3:** Evolution of the excess donors during annealing of the FZ silicon irradiated with 1.8 MeV protons to a fluence of 5x10^10 cm^-2. Annealing temperatures 125 to 500°C, step 25°C – results of C-V.

**Fig. 4:** Evolution of the excess donors during annealing of the FZ silicon irradiated with 1.8 MeV protons to a fluence of 5x10^12 cm^-2. Annealing temperatures 125 to 500°C, step 25°C – results of C-V.
Results and discussion

Evolution of free carrier (electron) profiles with annealing temperature in samples implanted with helium to fluences of $1 \times 10^9$ and $3 \times 10^{11} \text{cm}^{-2}$ is shown in Figs. 1 and 2, respectively. Both figures show that, up to 350 - 375°C, deep acceptors connected with radiation damage reduce donor doping close to the projected range $R_p$ of helium ions. For the higher fluence ($3 \times 10^{11} \text{cm}^{-2}$), this drop is followed by an artifact behaving as an excess donor doping behind the $R_p$ [3]. If annealing temperature exceeds 375°C and the majority of radiation, vacancy-related defects anneals out, the donor doping increases in the whole sample due to formation of TDs [4]. Their concentration peaks at 475°C and is remarkably enhanced at the place of the damage maximum. For the lower helium fluence (Fig. 1), the profile of these extra TDs follows well the distribution of radiation damage, while for the higher fluence (Fig. 2), the extra donor doping starts to grow from the irradiated surface and gradually extend up to the end-of-range of helium ions where it saturates at the level of $1.6 \times 10^{14} \text{cm}^{-3}$ and remarkably spreads.

Results of C-V measurement performed on proton irradiated samples (Figs. 3 and 4) show that hydrogen implantation leads to the formation of shallow donors whose concentration profile coincides with that of implanted hydrogen. Concentration of these shallow Hydrogen Donors (HDs) is proportional to the proton fluence. These centers are stable up to 100°C and are annealed out completely at about 250°C. SIMS data [5] showed that distribution of implanted hydrogen is stable up to the annealing temperature of 450°C, therefore the out diffusion of hydrogen atoms cannot be reason for annealing of these centers. It is more probable, that HDs annealing between 100 and 200°C occurs by their transformation to other defects containing hydrogen. Annealing of HD between 100 and 200°C is influenced by electric field. This is evidenced in Fig. 5 showing the influence of reverse bias applied on HD annealing at 125°C. While application of forward bias had no influence on HD distribution (not shown), increasing of the reverse voltage, i.e. spreading of the space charge region up to the range of implanted hydrogen, significantly reduced HD concentration. This effect can be explained by electric field of the SCR allowing drift of hydrogen ions or by the change of hydrogen charge state which results in different reaction constants for its interaction with other defects. Further annealing above 250°C leads to formation of shallow hydrogen donors (SHD) and hydrogen double donors (HDD) [6]. The net donor doping increases and its peak shifts closer to the surface (of about 1 µm) for both the lower and higher fluence. Since $\text{C}_7\text{-H}_2\text{O}_3$ complex was...
proposed as a possible core for SHDs in silicon [6], the enhanced formation of donor centers at radiation damage maximum in the temperature interval between 250 and 350 °C can be explained by annealing of radiation induced defects with subsequent formation C1-H-2O1 like complexes which is moderated by implanted hydrogen. Above 350 °C, the annealing characteristics are similar to those of helium implanted samples. This can be explained by annealing of SHD and HDD and parallel formation of TDs from radiation damage as in the case of the helium implantation. Fig. 6 shows that, at these annealing temperatures, the implantation of H or He with fluences producing equivalent radiation damage gives nearly identical TDs distribution.

Fig. 7 gives an overview about evolution of deep levels related to radiation damage during annealing of sample implanted with 1.8 MeV protons to a fluence of 5x10^{10} cm^{-2}. The identification parameters of detected levels and their attribution to lattice defects are in Table 1. Spectrum of the irradiated and unannealed (n.a.) sample contains peaks originating from typical radiation defects: the divacancy (E2, E4), vacancy-phosphorous (E4) and vacancy oxygen pair (E1). Additional deep levels (E3 and E5) are attributed to hydrogenated lattice defects: E3 to

![Fig. 7: DLTS spectra of the diode irradiated with 1.8 MeV protons to a fluence 5x10^{10} cm^{-2} (n.a.) and subsequently annealed up to 425°C (25°C step) - window of 260 s^{-1}.](image)

**Table 1.** Electron traps introduced in the FZ n-type silicon by proton irradiation (E1-E5) and subsequent annealing (A1-7).

<table>
<thead>
<tr>
<th>Level</th>
<th>Bandgap position (eV)</th>
<th>Capture cross section (cm^2)</th>
<th>Identity</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>E_C – 0.163</td>
<td>4x10^{15}</td>
<td>VO^{-0} + C_{2}C_{s}^{-0}</td>
</tr>
<tr>
<td>E2</td>
<td>E_C – 0.229</td>
<td>7x10^{15}</td>
<td>V_{2}^{0/-}</td>
</tr>
<tr>
<td>E3</td>
<td>E_C – 0.312</td>
<td>8x10^{16}</td>
<td>H-rel. (VO-H)</td>
</tr>
<tr>
<td>E4</td>
<td>E_C – 0.436</td>
<td>3x10^{15}</td>
<td>V_{2}^{0/-} + VP^{-0}</td>
</tr>
<tr>
<td>E5</td>
<td>E_C – 0.463</td>
<td>2x10^{16}</td>
<td>H-rel. (V_{2}H)</td>
</tr>
<tr>
<td>A1</td>
<td>E_C – 0.238</td>
<td>4x10^{15}</td>
<td>V_{2}O^{0/-}</td>
</tr>
<tr>
<td>A2</td>
<td>E_C – 0.454</td>
<td>7x10^{15}</td>
<td>V_{2}O^{(-0)}</td>
</tr>
<tr>
<td>A3</td>
<td>E_C – 0.211</td>
<td>1x10^{14}</td>
<td>?</td>
</tr>
<tr>
<td>A4</td>
<td>E_C – 0.440</td>
<td>8x10^{15}</td>
<td>?</td>
</tr>
<tr>
<td>A5</td>
<td>E_C – 0.507</td>
<td>6x10^{17}</td>
<td>H-rel. ?</td>
</tr>
<tr>
<td>A6</td>
<td>E_C – 0.314</td>
<td>1x10^{16}</td>
<td>H-rel. ?</td>
</tr>
<tr>
<td>A7</td>
<td>E_C – 0.506</td>
<td>1x10^{15}</td>
<td>H-rel. ?</td>
</tr>
</tbody>
</table>
the hydrogenated vacancy oxygen pair VOH and E5 is tentatively connected to the hydrogenated divacancy V2H [7]. Annealing of radiation damage in proton irradiated samples is influenced both by the presence of interstitial oxygen and implanted hydrogen. First, the VP centre is annealed at 175°C and the peak of the E4 level decreases. Annealing at 225°C does not affect the signal of the level E1 (VO pair) while two divacancy related peaks E2 and E4 shift to A1 and A2. This shift is interpreted as annealing of V2 and formation of a new centre with two charge states located close to V^{0}\text{ }2\text{ }/\text{ }V^{\text{o}}\text{ }2. The new centre, which is identical with V2O complex [8], anneals out at 350°C. At 225°C, also E5 (V2H) anneals or transforms to the new hydrogen related level A5. With increasing annealing temperature, concentration of hydrogenated VO centers (E3) increases. Taking into account results of shallow donor profiling, it can be speculated that increasing concentration of hydrogenated VO centers is a result of HD transformation when released hydrogen reacts with defects containing oxygen (VO, C\text{6}) giving rise to both the deep (E3) and shallow (SHD, HDD) levels. Above 350°C, VO and V2O complexes are annealed with subsequent formation of multiple vacancy V\text{ }n\text{ }and VO\text{ }n complexes [9] exhibiting deep levels A3-A4. For low irradiation fluences, these centres remain strongly localized close to the alpha’s range where the initial radiation damage peaked[10]. Levels A3-A4 and related defects remain in the damaged region up to 430°C, kill carrier lifetime significantly and represent a relevant source of vacancies and oxygen necessary for local enhancement of TDs formation. Since the TDs enhancement is limited by oxygen content in the target, the profiles show spread out and saturation at the defect maximum if irradiating fluence increases (see Figs. 2 and 4). The change of TDs distribution at higher implantation fluences is given by the accumulation of vacancy related defects closer to the irradiation surface. DLTS spectra of helium implanted samples contain only levels E1, E2 and E4 (VO pair and divacancy) which anneal in the same way as described above [10].

As in the case of shallow donor levels, application of the reverse bias during annealing of samples implanted with hydrogen changes the structure and number of observed deep levels. This is shown in Fig. 8 where DLTS spectra recorded during series of annealing steps performed with and without the applied reverse bias are presented. Fig.8 show that annealing with applied voltage decreases the amplitude of the level E4. The level E4 recovers when the sample is annealed again without bias. Since the observed drop of the amplitude of the level E4 is equal to the contribution of VP centers (see decrease of the amplitude after annealing at 175°C in Fig.7), one can conclude that the observed effect is given by passivation of the VP pairs by implanted hydrogen which is stimulated by the applied electric field. Metastable behavior of hydrogen related defects is further
shown in Fig. 9 where DLTS spectra of the hydrogen implanted sample annealed at 150°C are presented. The spectra (a) and (b), which were recorded under different reverse bias (19 and 50V) exhibit significant differences. Since, for both magnitudes, the space charge region fully covered the range of radiation damage, they can be attributed to the effect of electric field. Two completely new, metastable levels A6 and A7 are then clearly resolved in the differential spectrum. Since we found no analogy in helium implanted samples, these levels were attributed to metastable radiation defects containing hydrogen. Similar levels were already reported in hydrogen implanted [11] or electron irradiated and chemically etched [12] oxygen-rich n-type silicon.

Summary
We analyzed formation of deep and shallow levels in oxygen-rich float-zone n-type silicon subjected to proton and helium implantation and subsequent annealing at fluences and temperatures used for lifetime reduction in power devices. Results show that formation and annealing of shallow and deep hydrogen-related levels are strongly influenced by electric field at annealing temperatures below 175°C. Between 225 and 350°C, hydrogen reacts with defects containing oxygen and gives rise to VOH and C-H2Oi complexes. Finally, at temperatures from 375 to 500°C, radiation damage produced either by hydrogen or helium implantation significantly stimulates thermal donor formation. While at low fluences, the concentration of TDs is proportional to hydrogen (helium) fluence, for higher fluences, TDs concentration saturates.

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References