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Citation: *AIP Conf. Proc.* **1321**, 257 (2011); doi: 10.1063/1.3548365

View online: <http://dx.doi.org/10.1063/1.3548365>

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Deep Doping Profiles in Silicon Created by MeV Hydrogen Implantation: Influence of Implantation Parameters

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Abstract. The impact of dose variations of protons implanted with energies in the MeV range on the concentration and depth distribution of hydrogen-related shallow donors in float zone and Czochralski silicon after annealing at 470 °C is examined with spreading resistance probe measurements. For moderate proton doses up to 10^{14} cm⁻², the measured effective carrier distribution in float zone silicon correlates with the calculated distribution of the primary radiation damage caused by the penetrating protons. With increasing doses above 10^{14} cm⁻², however, the effective carrier distribution significantly deviates from the distribution of the primary defects. Furthermore, the shape of the induced profiles in float zone and Czochralski silicon differ considerably. The effective carrier concentration at the maximum of the induced donor profile exhibits a linear dependency on the implanted dose after annealing around 370 °C, whereas this dependency becomes clearly sublinear when annealing at 470 °C. A temperature dependent model using two donor species is proposed which accounts for the different dose dependencies at the different annealing temperatures.

Keywords: Silicon, hydrogen, ion implantation, donors, dopant profiles

PACS: 71.55.Cn; 34.50.Bw; 85.40.Ry; 61.72.uf; 61.72.J

INTRODUCTION

Doping of silicon by proton implantation was first reported in the 1970s by Zohra et al. [1] and shortly after by Gorelkinskiĭ et al. [2]. Irradiation of crystalline silicon with protons in the energy range of keV to MeV and successive annealing at temperatures up to 500 °C induces shallow donor type defects [3, 4] with ionization energies of several 10 meV [5–7]. Previous investigations have shown that various different energy levels exist, depending on the temperature of the annealing step [6, 8]. For the hydrogen-related donors (HDs) to appear, crystal damage, typically induced by irradiation with light particles, and hydrogen must coincide in the silicon sample. The hydrogen may either preexist in the substrate, e.g., by growing the crystal in a hydrogen ambient [9], or be injected into the crystal after the irradiation, e.g., by exposure to a hydrogen-plasma [6, 10]. In the case of proton implantation, the radiation damage and the hydrogen are inserted simultaneously. The damage profile generated by the irradiation with protons in the energy range of MeV extends to several 10 μm to 100 μm below the surface, while the majority of the implanted protons come to rest around their projected range near the end of the damage profile. During the successive annealing step, the implanted hydrogen must be allowed to dif-

fuse through the damaged layer in order for the donor profile to fully extend towards the surface [11].

The impact of dose variations on the effective carrier concentration and depth distribution in float zone silicon are investigated. Additionally, differences between the resulting donor distributions in float zone and Czochralski silicon are discussed.

EXPERIMENTAL

In this work, commercially available phosphorus doped 120 Ωcm float zone (FZ) and boron-doped 1 kΩcm magnetic Czochralski (Cz) silicon wafers are used. The samples are oxidized before irradiation. The wafers are tilted by 7° from the <100>-direction and irradiated with protons in the energy range from 500 keV to 4 MeV with doses ranging from 3×10^{13} cm⁻² to 8×10^{14} cm⁻². After implantation, specimens of convenient size are cut from the wafers and are annealed under inert atmosphere or air in the temperature range of 250–500 °C. The resulting charge carrier profiles are characterized by two-point spreading resistance probe measurements (SRP). The conversion of the spreading resistance curves into their equivalent carrier concentration may underestimate the charge carrier concentration as the carrier mobility might be reduced by residual radiation damage.

FIGURE 1. Equivalent carrier concentration profiles in FZ and Cz Si, created by implanting protons at 2.5 MeV with different doses and successively annealing at 470 °C for 5 h. The actual substrate doping concentration in the bulk of each sample is subtracted from all experimental curves. The primary damage distributions for proton doses of $3 \times 10^{13} \text{ cm}^{-2}$ and $4 \times 10^{14} \text{ cm}^{-2}$ calculated by SRIM [12] and scaled down by a factor of 10^{-4} are shown as well.

RESULTS

Figure 1 shows HD profiles in FZ and Cz Si together with simulated distributions of the primary vacancies induced by the implantation. The vacancy distributions are simulated for proton doses of $3 \times 10^{13} \text{ cm}^{-2}$ and $4 \times 10^{14} \text{ cm}^{-2}$ and each scaled down by 10^{-4} . This arbitrary factor of 10^{-4} accounts for the fact that only a fraction of the induced primary damage ultimately contributes to the HDs. From Fig. 1 it can be seen that the simulated vacancy distribution bears a good resemblance to the experimental profiles gained by SRP for proton doses up to 10^{14} cm^{-2} in FZ Si after annealing at 470 °C. For proton doses above 10^{14} cm^{-2} , however, a divergence between the HD profile shape and the primary damage distribution becomes visible. While the effective carrier concentration at the irradiated surface increases linearly with the implanted

FIGURE 2. Equivalent carrier profiles created in FZ with and without pre-oxidation prior to proton implantations at 2 MeV with a dose of $8 \times 10^{14} \text{ cm}^{-2}$ and annealing at 350 °C for 5 h.

dose, the concentrations at greater depths are significantly lower than expected for a linear relationship. As a result, the sign of the concentration gradient between the surface and a depth of about 40 μm is inverted.

During the oxidation step prior to the implantation, oxygen diffuses several μm into the samples. Fig. 2 shows samples with and without an oxidation step, in order to examine whether the oxygen profile has an effect on the increase of the carrier concentration towards the surface seen in Fig. 1 (FZ, $4 \times 10^{14} \text{ cm}^{-2}$). In the irradiated region not filled with HDs, acceptor-like radiation defects appear. These defects lead to a type-conversion of the originally *n*-type high resistivity FZ Si into *p*-type conductivity. During the annealing step, the hydrogen diffuses through the irradiated region towards the surface [11]. Where hydrogen and radiation damage coincide, HDs are created and the doping is again inverted to *n*-type. The *p*- and *n*-type regions in Fig. 2 are connected via a *p-n* junction at ~30 μm. The *p*-type regions of the profiles in Fig. 2 are actually found to depend on the oxidation step. This is tentatively attributed to the indiffused oxygen profile suppressing the acceptor-like radiation defects. However, after a prolonged anneal, allowing the hydrogen to diffuse through the entire penetrated region towards the surface, the profiles are no longer found to differ. Thus, the increase of the equivalent carrier concentration towards the surface in FZ samples implanted with proton doses above 10^{14} cm^{-2} is not related to oxygen indiffused during the pre-oxidation step.

For a more quantitative analysis of the dose dependent profile shape, Fig. 3 depicts the concentration at the maximum of the distribution in samples implanted with different proton doses between $3 \times 10^{13} \text{ cm}^{-2}$ and $8 \times 10^{14} \text{ cm}^{-2}$. The data for the 470 °C anneals is collected from FZ and Cz samples. From this figure, a sublinear dependency of the maximum concentration $C_{s,\text{max}}$ on the implanted proton dose N_{p+} after annealing at 470 °C becomes obvious. The experimental data are approximated by the equation

$$C_{s,\text{max}}(470^\circ\text{C}) \propto N_{p+}^\gamma, \quad (1)$$

with $\gamma = 0.58 \pm 0.04$. In contrast to this, $C_{s,\text{max}}$ appears to be an almost linear function of the implanted dose after annealing at 370 °C, i.e.,

$$C_{s,\text{max}}(370^\circ\text{C}) \propto N_{p+}^\beta, \quad (2)$$

where $\beta = 0.92 \pm 0.1$.

The physical effect causing the observed sublinearity around the maximum of the induced HD profile after annealing at 470 °C is not clear. Due to the high local concentration of radiation damage, the local carrier mobility might be reduced. This would result in an underestimation of the actual carrier concentration by the SRP method. However, if this were the cause of the anomalous profile shape, the same effect should be expected to affect the dose dependency of samples annealed at 370 °C, which is not the case.

Another possible explanation might be a higher-order-dependency of the donor defect concentration on the local concentration of the primary radiation damage or the hydrogen concentration. Such an effect might be argued to result from an attachment of surplus radiation-induced point defects or hydrogen atoms to the donor complex, changing the position of the donor level in the band gap. For this explanation to be in accordance with Fig. 3, two hydrogen-related donor species with different thermal stabilities need to be postulated. The first species, contributing around 370 °C, scales linear with the proton dose. The introduction rate of the second species, contributing around 470 °C, drops with increasing proton doses as argued above, resulting in the sublinear dependency depicted in Fig. 3.

The implanted protons come to rest around R_p and subsequently begin to diffuse through the sample. The resulting depth distribution of the protons clearly deviates from the distribution of the radiation defects. If the observed sublinearity is caused by a higher-order-dependency on the hydrogen concentration instead of the damage concentration, the difference between the damage and the hydrogen profiles may explain the change of the profile shape depicted in Fig. 1.

The reported sublinearity might be connected with the observation of diminishing donor concentrations after a prolonged plasma exposure in samples irradiated beforehand with protons, reported by Job et al. [10]. The authors speculated that the decline of the HD concentration might be attributed to an over-decoration of the induced donors with hydrogen, making them electrically inactive. Furthermore, we have recently reported on a linear dependence of the maximum donor concentration on the helium dose in helium and hydrogen co-implanted samples after annealing at 470 °C [13]. This also supports the assumption that the introduction rate of the electrically active HDs at 470 °C is reduced by the elevated local hydrogen concentration rather than the local damage concentration.

Annealing studies of $C_{s,max}$ in samples implanted with different proton doses and energies show a good agreement when all data are normalized to the concentration gained with the particular implantation param-

FIGURE 3. Equivalent carrier concentrations at the maximum of the induced donor profiles in FZ and Cz Si implanted with different proton doses at 2.5 MeV and annealed at 370 °C and 470 °C for 5 h. The isochronal annealing series are fitted according to Eqs. (1) and (2).

ters and annealed at 470 °C. Figure 4 shows such normalized curves for implantations with different energies and doses into FZ and Cz Si. The experimental data is approximated by a spline function, which in turn may be adequately fitted by a model using two donor species, as postulated above. In the scope of this fitting model, each of the two species is assumed to be sufficiently represented by a Gaussian curve. The maximums of the two Gaussians representing the activation functions of the donors lie at 350 °C and 454 °C, respectively. The function representing the temperature-dependent activation of the induced HDs, made up by the sum of two Gaussians in this simple model, is in good agreement with the experimental curve (Fig. 4). In order to account for the different doping efficiencies at 370 °C and 470 °C, depicted in Fig. 3, the two Gaussians should scale according to Eqs. (2) and (1), respectively.

Figure 1 furthermore shows a donor profile recorded in Cz Si which clearly differs from the profile in FZ Si under the same implantation and annealing conditions. In comparison to the profile in FZ Si, the region between the irradiated surface and the main peak in the Cz sample shows a distinctly higher equivalent carrier concentration. Another difference is the second peak, visible in the Cz sample in Fig. 1 at $\sim 75 \mu\text{m}$. This feature is not observed in any FZ samples within this study. This peak shows only a very weak dependence on the proton dose. The maximum concentration of this peak is seen to increase by about 50 % when the implanted proton dose is increased from $3 \times 10^{13} \text{ cm}^{-2}$ to $4 \times 10^{14} \text{ cm}^{-2}$ (not shown). Furthermore, its position tends to shift toward greater depths as the proton dose is raised.

The differences of the measured profiles in FZ and Cz Si are assumed to be mainly connected to the higher oxygen content in the Cz material. In the entire irradiated region, the generation rate of oxygen thermal donors (TDs) may be increased due to the induced

FIGURE 4. Equivalent carrier concentrations at the maximum of the donor profiles created in FZ and Cz Si by different proton implantations and annealing for 5 h. All values are normalized with respect to the concentration gained at the particular implantation parameters after annealing at 470 °C. The mean values at each annealing temperature are connected by a spline function. The analytical approximation is discussed in the text.

radiation defects. Such radiation-enhanced thermal donors (RETDs) are not specific to proton irradiation, as TD profiles in Cz Si may as well be created by helium implantation [14]. The presence of hydrogen is another enhancement factor for the generation of TDs [15, 16]. Due to the enhanced diffusivity of oxygen in the presence of hydrogen [17], oxygen from the bulk of the Cz Si might diffuse towards the projected range of the implanted hydrogen forming TDs. This accumulation of TDs could cause the peak at 75 μm and might explain its observed behavior with the proton dose.

Figure 5 shows an isothermal annealing study at 485 °C in Cz Si. Independent of the implantation (at depths beyond $\sim 85 \mu\text{m}$), the weak boron-doping of the Cz sample is overcompensated by TDs generated during annealing at 470 °C and, hence, the initial p -type conductivity is inverted to n -type. At 485 °C, however, the TDs responsible for the type-conversion in the bulk have begun to dissociate, and, as the annealing time is increased, the original p -type conductivity in the bulk is restored. Figure 5 shows that the additional TDs around 75 μm as well as in the penetrated range have likewise begun to anneal out, whereas the HDs prevailing in the main peak at 68 μm are still stable. The absolute decrease of the effective carrier concentration in the second peak and the penetrated region are quite equal, both being about $2 \times 10^{13} \text{ cm}^{-3}$ per time step. The additional TDs are presumably limited by the oxygen content in the Cz Si and, therefore, become irrelevant, as they are outnumbered by HDs, e.g., in the main peak. Hence, at the maximum of the profiles, the effective carrier concentration is not significantly influenced by the choice of the crystal type, i.e., FZ or Cz Si.

FIGURE 5. Profiles of the equivalent carrier concentration in Cz Si created by implanting protons with 2.5 MeV and a dose of $1 \times 10^{14} \text{ cm}^{-2}$ and isothermally annealing at 485 °C. The simulated distribution of the primary defects is shown in arbitrary units for comparison.

CONCLUSION

The impact of dose variations on effective carrier profiles induced by proton implantation is discussed. In the case of implantations into FZ Si, the effective carrier profiles show a good correlation with the induced radiation damage distribution only for doses up to 10^{14} cm^{-2} . It is found that the effective carrier con-

centration at the maximum of the distribution exhibits a clearly sublinear dependency on the implanted dose in the investigated range for an annealing temperature of 470 °C and is rather independent of the silicon substrate. It is proposed that the decline of the introduction rate of the hydrogen-related donors with increasing proton doses is related to the increase of the local hydrogen concentration. Pronounced differences between the profile shape in FZ and Cz Si are discussed and attributed to the enhanced generation of thermal oxygen donors in Cz Si showing a different annealing behavior than the hydrogen-related donors.

ACKNOWLEDGMENTS

This project is financially supported by the European Center for Power Electronics (ECPE) and Infineon Technologies AG. Helpful discussions with Prof. R. Job regarding the peak beyond the maximum emerging in Cz Si are gratefully acknowledged.

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