

Proton implantation in silicon: evolution of deep and shallow defect states

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The effect of proton implantation on enhanced formation and evolution of deep and shallow defects levels was investigated in float-zone and Czochralski n-type silicon. Implantation was performed with 700 keV and 1.8 MeV protons to fluences ranging from 7×10^9 to $5 \times 10^{13} \text{ cm}^{-2}$. Implanted samples were isochronally annealed up to 500°C. Introduced radiation defects and shallow donors were investigated by DLTS and CV profiling. The results show that proton implantation leads to introduces hydrogen donors (HDs) at the proton end-of-range in both materials. The introduction rate of HDs is proportional to implantation fluence and HDs formation is substantially enhanced in Czochralski silicon. HDs anneal out when annealing temperature exceeded 250 °C. At higher temperatures, thermal shallow hydrogen donors (SHD) and thermal donors (TDs) are generated. While in float-zone material TDs form only at the damage maximum, in Czochralski silicon their distribution spreads on both sides for annealing temperatures higher than 400 °C.

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1. Introduction

Nowadays, implantation of silicon with high energy light ions is a widely used tool for arbitrary lifetime control in silicon power devices [1]. The implantation introduces point-like defects locally. Recombination of excess carriers therefore proceeds only where it is necessary and device switching speeds up without significant deterioration of other parameters. Excluding alphas, a considerable attention is still paid to implantation of protons since it brings longer projection ranges, lower leakage and also opens possibility of low temperature doping of silicon by hydrogen related donors [2]. The implanted devices are subsequently annealed to stabilize unstable fraction of vacancy-related defects and remove undesirable ones. During the annealing, new defects are created as a result of interaction of vacancy related defects, implanted protons and intrinsic defects in silicon.

In the present paper, we study the effect of proton implantation and subsequent isochronal annealing on formation of defects giving rise to deep and shallow levels in silicon bandgap. The study is performed on both the float-zone and Czochralski n-type silicon.

2. Experimental

Evolution of deep and shallow levels was studied on several type of silicon substrates. Firstly, the low-doped (phosphorous concentration below 10^{14} cm^{-3}) <100> oriented FZ n-type silicon forming the n-base of the planar p^+nn^+ diodes was used. The diodes has a relatively high concentration of oxygen since their deep p^+ and n^+ emitters were produced by long thermal diffusion. The diodes were

implanted by 1.8 MeV protons at fluences ranging from 7×10^9 to $5 \times 10^{12} \text{ cm}^{-2}$. Another test structures were p^+nn^+ diodes based on low-doped <111> FZ silicon with shallow p^+ and n^+ emitters that guaranteed low oxygen concentration in the n-base. The same structure based on Czochralski <111> n-type silicon were also prepared. The diodes with shallow anode emitter were implanted by 700 keV protons at wide range of fluence from 1×10^{10} to $5 \times 10^{13} \text{ cm}^{-2}$. Due to different implantation facility, the implantation of diodes with shallow emitter was performed at zero degree in respect of incoming ion beam while the diodes with deep emitters were implanted at 7°. After implantation, isochronal (30 minutes) annealing in the air in temperature range from 100 to 500°C was applied. Deep levels resulted from implantation and the subsequent isochronal annealing were monitored by deep level transient spectroscopy using DLS-82E and DLS-83E spectrometers. Profiles of shallow levels were characterized using HP 4280 1MHz capacitance analyzer at temperature 85°C to eliminate influence of ionized deep acceptors [3]. To monitor influence of radiation centers on leakage of modified structure curve tracer was also used. Leakage current of samples was monitored at 85°C at reverse voltage of 100V.

3. Results and discussion

Deep levels. Spectra corresponding to radiation defects appearing after implantation with 700 keV protons to fluences ranging from $1 \times 10^{11} \text{ cm}^{-2}$ to $1 \times 10^{12} \text{ cm}^{-2}$ are shown in Fig. 1. One can see five major peaks that correspond to different deep levels in silicon bandgap.

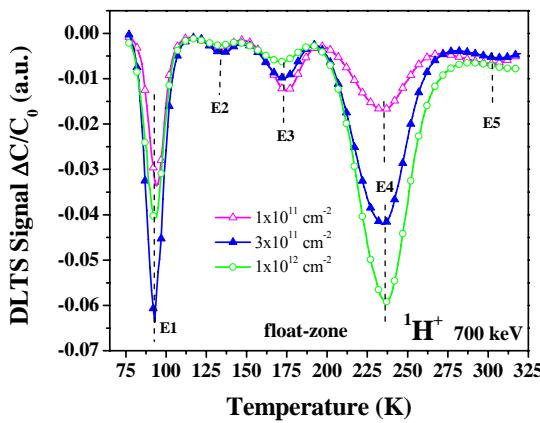


Fig. 1. DLTS spectra of the $p^{+}nn^{+}$ diode (float-zone) irradiated with a 700 keV $^{1}H^{+}$ ions to a fluence from $1 \times 10^{11} \text{ cm}^{-2}$ to $1 \times 10^{12} \text{ cm}^{-2}$ measured under majority carrier injection (rate window 260 s^{-1}).

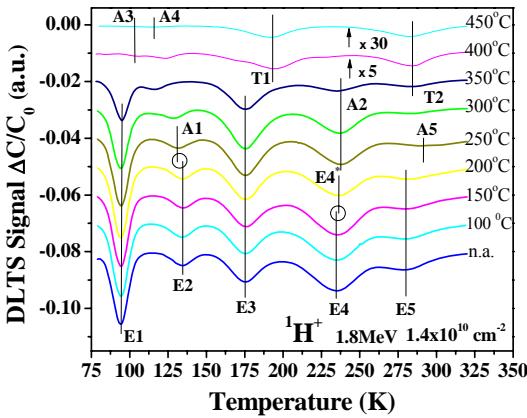


Fig. 2. Evolution of deep levels in oxygen-rich float-zone silicon promoted by isochronal annealing. Sample irradiated with 1.8 MeV protons to fluence of $1.4 \times 10^{10} \text{ cm}^{-2}$ Rate window of 260 s^{-1} .

They are attributed to the following defects: the vacancy-oxygen pair $\text{VO}^{(-/0)}$ at $E_{\text{C}}-0.163\text{eV}$ (E1), the double charge state of divacancy $\text{V}_2^{(-/-)}$ at $E_{\text{C}}-0.252\text{eV}$ (E2), the hydrogenated vacancy-oxygen pair VO-H at $E_{\text{C}}-0.312\text{eV}$ (E3), the single negative state of divacancy $\text{V}_2^{(-/0)}$ with a contribution the acceptor level of vacancy-phosphorous pair (E-center, $\text{VP}^{(-/0)}$) at $E_{\text{C}}-0.436\text{eV}$ (E4) and an unknown defect at $E_{\text{C}}-0.463 \text{ eV}$ (E5) which is sometimes connected with hydrogenated divacancy V_2H . None of these levels was detected in diodes before the irradiation. The same radiation defects were also detected in proton irradiated Czochralski silicon (not shown). Fig. 1 shows that irradiation to higher fluences does not add any new levels to majority spectra, however it changes defect introduction rate if we compare the height of DLTS peaks

corresponding to particular defects. It can be concluded that up to the fluence of $3 \times 10^{11} \text{ cm}^{-2}$ the concentration of VO and $\text{V}_2\text{-VP}$ complexes increase proportionally to applied fluence. Up to this fluence, the efficient trapping of O_i by single vacancies results in enhanced formation of VO center and its concentration prevails compared to other defects. At fluence of $1 \times 10^{12} \text{ cm}^{-2}$, one can see that formation of VO is lower as expected and its further increasing is limited by finite source of O_i . For VOH complex, the effect was already observed at fluence of $3 \times 10^{11} \text{ cm}^{-2}$.

Evolution of deep defect states. DLTS spectra of majority carrier traps resulting from implantation with 1.8 MeV protons (n.a.) and subsequent isochronal 30 min annealing in the range from 100°C to 450 °C are shown in Fig. 2. The dependence of the DLTS peak amplitude versus annealing temperature resulting from the Fig. 2 is plotted in Fig. 3. One can see from the Fig. 3 that slight decreasing in concentration of VO complex already occurs at 150°C. At the same temperature, the concentration of hydrogenated vacancy-oxygen pairs VOH increases. At 150°C, the E-center also starts to anneal. As a result decreasing in amplitude of peak E4 which corresponds to $\text{V}_2\text{-VP}$ occurs. If we assume that all E-centers are annealed out at 175°C according to reaction $(\text{VP} \leftrightarrow \text{V} + \text{P})$, the magnitude of peak E4^{*} measured after annealing at 200°C corresponds to concentration of $\text{V}_2^{(-/0)}$. Analysis of DLTS spectra (see Fig. 2) allows us to conclude that approximately 8% of E-center contributes to E4. A slight shift of E4^{*} and E2 peaks was revealed after 220 °C and this shift is attributed to formation of $\text{V}_2\text{O}^{(-/-)}$ and $\text{V}_2\text{O}^{(-/0)}$ [4]. Fig. 3 shows that concentration of these centers is lower compared to $\text{V}_2^{(-/-)}$ and $\text{V}_2^{(-/0)}$. Part of divacancy can also react with hydrogen to form electrically neutral V_2H_2 complex.

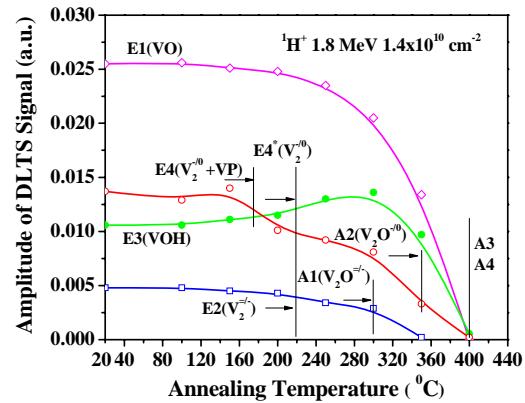


Fig. 3. Amplitude of DLTS signal for several recombination centers in silicon after irradiation with 1.8 MeV protons to fluence $1.4 \times 10^{10} \text{ cm}^{-2}$ and consequent isochronal annealing. Proposal defect identification is shown in brackets.

Table 1. Electron traps detected in the $^1\text{H}^+$ irradiated FZ silicon after isochronal annealing

| Level | Bandgap Position (eV) | Capture Cross Section (cm^2) | Identity |
|-------|-----------------------|---|----------------------------|
| E4* | $E_C-0.425$ | 1.8×10^{-15} | $\text{V}_2^{(-)}$ |
| A1 | $E_C-0.238$ | 4×10^{-15} | $\text{V}_2\text{O}^{(=)}$ |
| A2 | $E_C-0.454$ | 7×10^{-15} | $\text{V}_2\text{O}^{(-)}$ |
| A3 | $E_C-0.181$ | 5×10^{-15} | ? |
| A4 | $E_C-0.211$ | 9.6×10^{-15} | ? |
| A5 | $E_C-0.507$ | 6×10^{-17} | ? |

The levels arisen during post-implantation annealing and their electrical parameters received from DLTS measurements are collected in Table 1. In the case shown in Fig. 2 the spectra detected after annealing at 400 °C contains only negligible signal from levels A3 and A4 while all vacancy related radiation defects resulted from irradiation are completely annealed. It is also worth to mention that at higher implantation fluences, the center A4 becomes a significant recombination center due to its high thermal stability. For fluences above 10^{11} cm^{-2} , its concentration remains high even after annealing at 500 °C. The center was also detected in alpha irradiated samples [5].

Generation current of diodes implanted by 700 keV protons to fluence of $3 \times 10^{12} \text{ cm}^{-2}$ is shown in Fig. 4 as function of annealing temperature in the range from 85°C to 500 °C for both float-zone and Czochralski materials. Fig. 4. shows that concentration of generation centers in Czochralski material is approximately 1.2 times higher than in float-zone material for the same proton fluence. It demonstrates sharply decreasing by annealing below 225°C for both samples. One can attribute a part of the decreasing to annealing of E-center. In the annealing interval from 225°C mainly $\text{V}_2\text{O}^{(-)}$ center participate to current generation. It anneals after 350°C and reverse current monotonically decreases since most of vacancy related generation centers are swept by annealing temperature.

Influence of electric field. The reverse bias applied during isochronal annealing can influences the amount of observed radiation defects. This situation is depicted in Fig. 5 where DLTS spectra were recorded on sample implanted with 1.8 MeV to fluence $7 \times 10^9 \text{ cm}^{-2}$. Several annealing were performed with and without applied reverse voltage. One can see from Fig.5 that annealing with applied voltage decreases the amplitude of the level E4. Its amplitude recovered when the sample was annealed without bias again. We can notice equivalent drop of the amplitude of the level E4 which corresponds to the contribution of VP centers (see decrease of the amplitude after annealing at 175°C in Fig.2). It is possible that the passivation the VP centers by hydrogen stimulated by electric field occurs in this case.

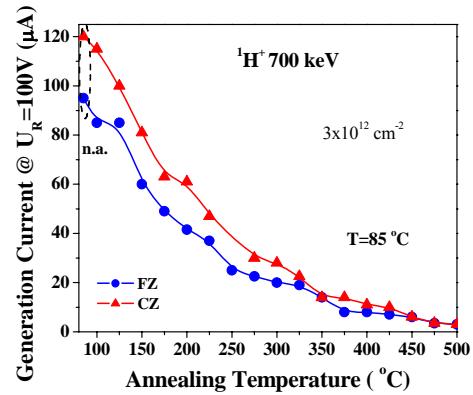


Fig. 4. Generation current versus annealing temperature for float-zone and Czochralski based diodes irradiated with 700 keV protons to fluence of $3 \times 10^{12} \text{ cm}^{-2}$.

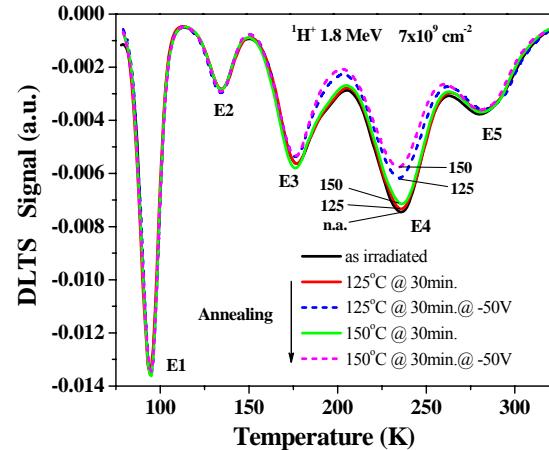


Fig. 5. DLTS spectra of the proton (1.8 MeV $7 \times 10^9 \text{ cm}^{-2}$) irradiated silicon annealed with and without applied reverse bias.

Evolution of shallow defect states. Irradiation with hydrogen leads to formation of shallow hydrogen donors (HDs). Their distribution coincides with distribution of implanted hydrogen. An example of the HDs distribution is shown in Fig. 6 for sample irradiated with 1.8 MeV at fluence $5 \times 10^{12} \text{ cm}^{-2}$. One can see that maximum HDs concentration occurs after irradiation and they annealed at about 250 °C probably by transformation to other defects containing hydrogen. This assumption correlates with result of DLTS measurement (see Fig. 3) that showed increasing of VOH concentration in this temperature range. Annealing at temperature above 250 °C give a rise to shallow hydrogen donors (SHD) and hydrogen double donors (HDD) [6]. They posses the highest concentration between 250 and 350 °C. This process is connected with annealing out of radiation defects and their participation to formation of SHDs. At higher temperatures they anneal out and thermal donors (TDs) start to appear and spread

into the whole bulk of irradiated structure which is free from radiation damages. The TDs achieved maximal concentration at about 475 °C and start to anneal at 500 °C.

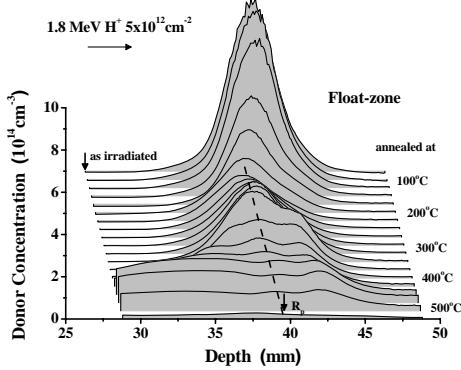


Fig. 6. Evolution of the excess donors during annealing of the FZ silicon irradiated with 1.8 MeV protons to a fluence of $5 \times 10^{12} \text{ cm}^{-2}$.

The situation differs when proton irradiation is applied to sample with shallow emitters i.e. with low oxygen content material. This case is shown in the Fig. 7 for float-zone based structure irradiated by protons with 700 keV at fluence $1 \times 10^{13} \text{ cm}^{-2}$. Since the irradiation was performed at 0° in respect of protons beam one can speculate that some fraction of impinging protons participated to channeling. That is why the shape of HDs distribution deviates from Gaussian like. As well as for the situation shown in Fig. 6, the SHD begin to disappear at 350 °C and TDs form only close to end-of-range of protons. At temperature 400 °C they possess the maximum concentration and moderate radiation damages towards to irradiated surface. One can conclude that in this case low oxygen in the material do not allow starting of TDs in the bulk as in case showed in Fig. 6. At temperatures higher than 400 °C these TDs formed by the assistance of radiation damage gradually anneal out.

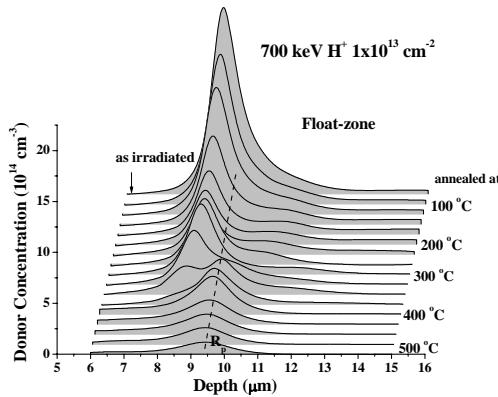


Fig. 7. Evolution of the excess donors during annealing of the FZ silicon irradiated with 700 keV protons to a fluence of $1 \times 10^{13} \text{ cm}^{-2}$.

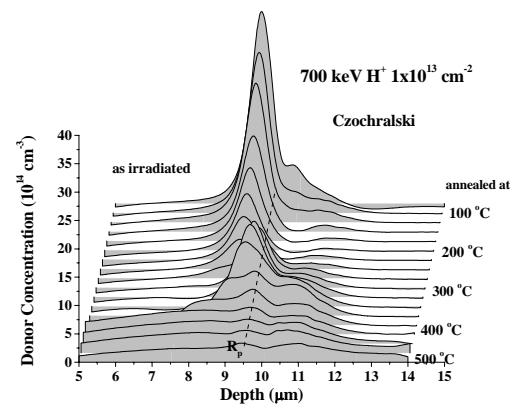


Fig. 8. Evolution of the excess donors during annealing of the Czochralski silicon irradiated with 700 keV protons to a fluence of $1 \times 10^{13} \text{ cm}^{-2}$.

In Fig. 8 evolution of excess donors is shown for Czochralski material irradiated by 700 keV with fluence of $1 \times 10^{13} \text{ cm}^{-2}$. Here, one can see that after annealing of HDs the new shallow hydrogen donors started with a peak shifted towards to R_p . Further annealing above 350°C stimulates broadened distribution of TDs not only toward irradiated surface but also into the bulk. This confirms the assumption that higher concentration of intrinsic impurities in Czochralski material enhances evolution of excess TDs. Fig. 9 shows HD sheet concentration versus proton fluence for this experiment and compares it with literature data [7]. One can see that HDs concentration is linearly proportional to the proton fluence in wide fluence range for both FZ and Czochralski materials. Excess intrinsic impurities in Czochralski silicon determines higher introduction rate of HD in this material.

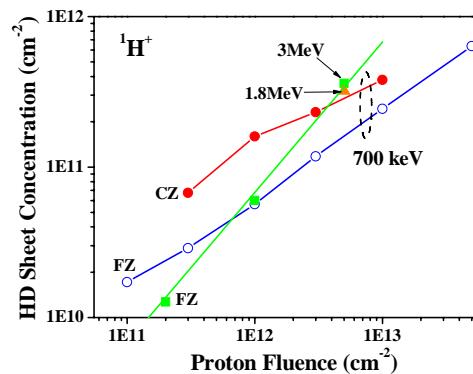


Fig. 9. The sheet concentration of hydrogen donors obtained from C-V measurement for different materials as a function of proton fluence.

4. Conclusions

The effect of proton implantation on enhanced formation and evolution of deep and shallow defect states was investigated in n-type oxygen-reach and oxygen-lean

FZ silicon as well as for Czochralski silicon. It was shown that electric field applied during isochronal annealing below 175°C significantly affects annealing of the level E4 which is probably caused by metastable passivation of vacancy-phosphorous pair. After proton implantation into all materials, the enhanced formation of hydrogen donors (HDs) was observed at the proton end-of-range. The introduction rate of HDs was enhanced in Czochralski material and it was attributed to higher concentration of intrinsic impurities in the material. Concentration of HDs increased linearly to irradiation fluences. In oxygen-lean material formation of TDs was limited and no generation of TDs in the bulk occurred.

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