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Abstract
Deep donor layers were investigated in silicon p⁺nn⁺ diodes after implantation with 700 keV protons, subsequent treatment in rf hydrogen plasma and isochronal annealing up to 500ºC on air. Two types of diodes fabricated from oxygen-lean float-zone and oxygen-rich Czochralski silicon substrates were used. Effect of hydrogen plasma on radiation defect evolution was monitored by deep level transient spectroscopy and deep donor layers were characterized by C-V profiling. Results demonstrate that hydrogen plasma efficiently removes majority of vacancy-related defects resulted from proton implantation in both silicon substrates. Both the plasma treatment and post-implantation annealing lead to appearing of new defects in silicon band gap. In contrast with reference samples without plasma treatment, the treated samples with equivalent proton fluence demonstrate higher concentration of the residual damages, which increase with annealing temperature and, hence, lead to reduction of minority carrier lifetime. Simultaneously, hydrogen plasma deteriorates electrical properties of thermal hydrogen-related shallow donors. Concentration of hydrogen-related donors decreased after plasma-treatment compared to as-implanted samples. Development and shift of donor distributions detected by C-V measurement during subsequent annealing was attributed to shift of p-n junction depth. It was demonstrated that hydrogenated samples suffered from enhanced leakage current that remains high even after annealing at 400ºC.

Keywords: Silicon, thermal donors, hydrogen plasma, implantation, protons, lifetime control.

INTRODUCTION
Recently, proton implantation into silicon followed by low-temperature annealing was demonstrated to produce local donor layers at the proton end-of-range [1-2]. The so-called hydrogen-related thermal donors (THDs) arise at temperature above 350ºC and their formation is moderated by both radiation defects and hydrogen ions. It was reported that generation of THDs strongly depends on used starting material and post-implantation processing [3-4]. Since THDs are complex crystalline defects that exist in relatively narrow temperature range (up to 600ºC) and their maximum concentration is limited to approximately 1x10¹⁶ cm⁻³, they can not replace n-type doping made by high temperature diffusion of phosphorous or arsenic [5-7]. However, this technique proposes high precision of donor localization which is predefined by proton energy and can vary from subsurface region to hundreds of micrometers. The effort to achieve higher donor concentration is faced with residual implantation damage that significantly reduces carrier lifetime. Recently, use of radio frequency (rf) hydrogen plasma inserted prior to post-implantation annealing was also demonstrated as promising approach for n-type doping in modern power devices [8-9]. It is expected that hydrogen plasma could improve quality of the THDs layers.

In this contribution we present results of investigation on low-temperature formation of n-layer by proton implantation and compare two-step processing (proton implantation → annealing) with three-step processing technique (proton implantation → hydrogen RF plasma treatment → annealing). Effect of hydrogen plasma was investigated on n-type FZ silicon with low oxygen concentration and oxygen-rich n-type Czochralski silicon.

EXPERIMENTAL
Two types of silicon substrate were chosen for the experiment. First material was the low-doped n-type (phosphorus concentration 9x10¹³ cm⁻³) <111> oriented float-zone (FZ) silicon with low oxygen concentration ([O⁺]~2x10¹⁶ cm⁻³). The second material was Czochralski (CZ) <111> n-type (phosphorus concentration 6x10¹⁴ cm⁻³) oxygen-rich ([O⁻]~1.4x10¹⁸ cm⁻³). Identical p⁺nn⁺ planar chip diodes were fabricated from the substrates. Diodes were made with shallow p⁺ and n⁺ emitters (~1µm) and had no metallic contact to allow effective plasma treatment. The diodes were implanted from p⁺ anode side with 600 keV protons to fluence 1x10¹⁰ cm⁻².
and 700 keV protons to fluence ranging from $1 \times 10^{13}$ to $3 \times 10^{14}$ cm$^{-2}$ using 3MV Tandetron accelerator. According to SRIM2008 simulation, the chosen energies produced proton distribution with maximum concentration in depths of approximately 7.8 and 9.7 μm, respectively. Hydrogen rf plasma (13.56 MHz) with supplied power 250 W was applied to introduce hydrogen into implanted samples at substrate temperature of approximately 250-280°C. Part of implanted samples was left without the plasma treatment. Reference and hydrogenated samples were isochronally annealed in temperature range from 100 to 500°C on air. Deep levels resulted from proton implantation, plasma treatment and isochronal annealing were monitored by deep level transient spectroscopy (DLTS). The profiles of deep donor layers were received from capacitance-voltage (C-V) measurement. To eliminate influence of ionized deep acceptors from donor distribution, all the C-V characteristics were recorded when samples were heated at 85°C [10]. Diode leakage was monitored at 85°C and reverse voltage of 100V. OCVD technique was applied to measure carrier lifetime.

RESULTS AND DISCUSSION

Effect of hydrogen plasma on radiation defects

DLTS spectra recorded on FZ and CZ silicon samples after implantation with 600 keV protons to fluence $1 \times 10^{10}$ cm$^{-2}$ and treated in hydrogen plasma are collected in Fig. 1 after implantation with 600 keV protons to fluence $1 \times 10^{10}$ cm$^{-2}$. DLTS spectra recorded on FZ and CZ silicon samples and 700 keV protons to fluence ranging from $1 \times 10^{13}$ to $3 \times 10^{14}$ cm$^{-2}$ using 3MV Tandetron accelerator. According to SRIM2008 simulation, the chosen energies produced proton distribution with maximum concentration in depths of approximately 7.8 and 9.7 μm, respectively. Hydrogen rf plasma (13.56 MHz) with supplied power 250 W was applied to introduce hydrogen into implanted samples at substrate temperature of approximately 250-280°C. Part of implanted samples was left without the plasma treatment. Reference and hydrogenated samples were isochronally annealed in temperature range from 100 to 500°C on air. Deep levels resulted from proton implantation, plasma treatment and isochronal annealing were monitored by deep level transient spectroscopy (DLTS). The profiles of deep donor layers were received from capacitance-voltage (C-V) measurement. To eliminate influence of ionized deep acceptors from donor distribution, all the C-V characteristics were recorded when samples were heated at 85°C [10]. Diode leakage was monitored at 85°C and reverse voltage of 100V. OCVD technique was applied to measure carrier lifetime.

RESULTS AND DISCUSSION

Effect of hydrogen plasma on radiation defects

DLTS spectra recorded on FZ and CZ silicon samples after implantation with 600 keV protons to fluence $1 \times 10^{10}$ cm$^{-2}$ and treated in hydrogen plasma are collected in Fig. 1 and Fig. 2 respectively. Spectra measured on reference samples subjected only to proton implantation are also shown. DLTS spectra of both FZ and CZ reference sample exhibit four majority peaks E1-E4 that correspond to different deep traps in silicon band gap. Their identification and measured parameters are given in Table 1. The level E5 which is sometimes attributed to hydrogenated divacancy was detected only in FZ samples. DLTS spectra of the as irradiated samples on Figs. 1 and 2 show different proportions in peak height. This is given by different O$_i$ concentration and doping in FZ and CZ substrates. Equivalent DLTS signal for CZ sample represents 5 times higher concentration of VOH centers compared to FZ silicon. The results presented in Figs. 1 and 2 show an interaction between existing radiation defects and hydrogen introduced from rf plasma. It is evident that 60 min. plasma treatment caused a strong effect of defect neutralization in both FZ and CZ materials. The peaks E1, E2, E4 and E5 completely disappeared from the spectra. Only peak E3 remains almost unchanged after hydrogenation in FZ silicon and its concentration 1.8 times increased in CZ material. New, hydrogen related peak P1 appeared on both DLTS spectra. Level P2 starts to develop in spectrum of CZ sample and its concentration increases with proton fluences in both materials. The level P2 was also registered after hydrogenation of silicon substrates previously subjected to helium irradiation on the same structures [11]. Results demonstrate that plasma treatment can significantly influence electrical properties of the radiation defects and passivates most important in respect of carrier recombination levels E1 and E4. Profiles of VOH centers (E3) received on hydrogenated and as irradiated FZ samples showed almost identical distribution which is localized close the projected proton range in both cases. Increasing of the E3 peak in spectrum recorded on CZ silicon is given by the additional hydrogen in-diffusing from plasma treated surface. Since the oxygen content is substantially lower in FZ silicon, this effect is not observed in FZ substrate. Diffusing hydrogen mostly exist in forms of interstitial molecules in silicon therefore passivation of VO centers can be explained by formation of electrically neutral VOH$_2$ complex. During this reaction mobile hydrogen molecules are captured by VO [12]. One can speculate that the peak P1 formed by plasma treatment can contain complex of divacancy and hydrogen atoms $V_2H_n$ ($n=2,…,6$) which is believed to be electrically active in silicon except of fully saturated $V_2H_6$ complex. The level P2 was observed previously in irradiated silicon doped by H [13] and was attributed to complex containing VO center and H (VOH$^+$). This complex is less stable than VOH center and a continuous supply of hydrogen is
required to maintain its concentration high. It is important to underline P1 and P2 levels were not registered in DLTS spectra of FZ and CZ material without previous implantation. The DLTS spectra in Figs. 1 and 2 show that effect of plasma on radiation defects introduced by relatively low proton fluence. However, for effective generation of excess THDs, the fluences exceeding $1 \times 10^{13}$ cm$^{-2}$ are required. The DLTS technique is capable to give rigorous results only if defect concentration is much lower compared to the doping of n-base. Therefore, post-implantation annealing is required to the use of DLTS. Fig. 3 shows the DLTS spectra measured on reference FZ substrates implanted with 700keV proton to fluence $1 \times 10^{13}$ cm$^{-2}$ and annealed at 400 and 450ºC respectively. Spectra measured on identically implanted and treated by plasma samples are shown in Fig. 4. Since magnitude of DLTS peak is proportional to corresponding defect concentration, one can notice significant difference between defect concentration of reference and plasma treated samples. After annealing, several new levels labeled as A1-A7 were detected in DLTS spectra. Their identified parameters are collected in Table 1. The levels A1, A2, A3 and A4 appeared in both samples, while the levels A5, A6 and A7 arose only in plasma treated material. In plasma treated sample, annealing of the peak A5 is accompanied with reappearance of peak E3 which corresponds to VOH centers. In reference sample, one can also notice increasing of E3 peak with corresponding decrease of A1 peak. It is evident that hydrogen introduced by plasma treatment promotes different reactions of radiation defects compared to reference sample. It is important to note that the rf plasma power used in our experimental setup was rather aggressive (250 W). Therefore, a number of specific structural defects included voids, dislocation loops, platelets etc. can develop after plasma treatment and subsequent annealing. These defects contain vacancies and interstitials and can

<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>$E_C - 0.167$</td>
<td>$\sigma_n = 2 \times 10^{-15}$</td>
<td>VO$^{+}$</td>
</tr>
<tr>
<td>E2</td>
<td>$E_C - 0.252$</td>
<td>$\sigma_n = 7 \times 10^{-15}$</td>
<td>V$_2^{+}$</td>
</tr>
<tr>
<td>E3</td>
<td>$E_C - 0.312$</td>
<td>$\sigma_n = 1 \times 10^{-15}$</td>
<td>VOH$^+$</td>
</tr>
<tr>
<td>E4</td>
<td>$E_C - 0.436$</td>
<td>$\sigma_n = 3 \times 10^{-15}$</td>
<td>V$^+_1$(PV)</td>
</tr>
<tr>
<td>E5</td>
<td>$E_C - 0.496$</td>
<td>$\sigma_n = 2 \times 10^{-16}$</td>
<td>V$_2^+(PV)$</td>
</tr>
<tr>
<td>P1</td>
<td>E0</td>
<td>$\sigma_n = 9 \times 10^{-14}$</td>
<td>H-rel</td>
</tr>
<tr>
<td>P2</td>
<td>E$_C - 0.365$</td>
<td>$\sigma_n = 5 \times 10^{-15}$</td>
<td>VOH$^*$</td>
</tr>
<tr>
<td>A1</td>
<td>E$_C - 0.177$</td>
<td>$\sigma_n = 8 \times 10^{-15}$</td>
<td></td>
</tr>
<tr>
<td>A2</td>
<td>E$_C - 0.295$</td>
<td>$\sigma_n = 8 \times 10^{-14}$</td>
<td></td>
</tr>
<tr>
<td>A3</td>
<td>E$_C - 0.408$</td>
<td>$\sigma_n = 3 \times 10^{-15}$</td>
<td></td>
</tr>
<tr>
<td>A4</td>
<td>E$_C - 0.429$</td>
<td>$\sigma_n = 2 \times 10^{-14}$</td>
<td></td>
</tr>
<tr>
<td>A5</td>
<td>E$_C - 0.276$</td>
<td>$\sigma_n = 2 \times 10^{-15}$</td>
<td></td>
</tr>
<tr>
<td>A6</td>
<td>E$_C - 0.211$</td>
<td>$\sigma_n = 1 \times 10^{-14}$</td>
<td></td>
</tr>
<tr>
<td>A7</td>
<td>E$_C - 0.448$</td>
<td>$\sigma_n = 1 \times 10^{-15}$</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Survey of identification parameters of deep levels. Labels: E-implanted samples, P-plasma treated, A-annealed.
extend from the treated surface to subsurface region. This situation is shown in Fig. 5, which demonstrates depth distribution of the level A5 detected in hydrogenated FZ silicon after annealing at 400ºC. The defect distribution shows its maximum close to projected range of protons and its tail region significantly enhances towards to hydrogenated surface. There is no direct measurement on hydrogen distribution in subsurface region in this work. However, according to several investigations of hydrogen plasma treated, silicon it is known that diffusion length of positively charged protons can vary up to 10 µm at 200ºC [14]. This diffusion parameter can be limited due to hydrogen interaction with extended defects formed by plasma treatment, oxygen, dopants, etc. The hydrogen diffusion is also accompanied with hydrogen self-interaction resulting in formation of interstitial molecules. According to SIMS measurement on hydrogen implanted and annealed silicon, profile of hydrogen remains localize in vicinity of projected range up to 500ºC [4]. Results of SIMS measurement gathered from deuterized FZ samples showed strong dependence of hydrogen concentration on sample temperature during plasma treatment [14]. Thus, the highest subsurface concentration of deuterium was observed at level $1 \times 10^{17}$ cm$^{-3}$ at substrate temperature of 200ºC and it decreased to level $1 \times 10^{15}$ cm$^{-3}$ at depth ~ 10 µm. Sample temperature in our case was approximately 250ºC, therefore, we expect even higher hydrogen gradient in subsurface region because Raman investigations [15] showed maximum signal for interstitial hydrogen molecules at 250ºC. One can conclude that very complex defect reactions occur during plasma treatment and consequent annealing at surface and subsurface region. The situation showed in Figs. 3 and 4 is particular case that demonstrates defect reaction moderated by hydrogen diffusing from the surface, hydrogen in the region of projected range and defects resulted from proton implantation and plasma treatment.

**Formation of shallow hydrogen thermal donors**

Fig. 6 shows evolution of excess shallow donors in reference FZ samples subjected to 700 keV proton implantation with fluence $1 \times 10^{14}$ cm$^{-2}$ and subsequent annealing in range from 100 to 500ºC. The Gaussian-like profile of hydrogen donor (HDs) is introduced already after implantation. Since HDs exhibit maximum concentration in as implanted sample, it was not possible to fully trace their distribution before annealing because increased n-type concentration in the region of projected range acts as the stopping layer for penetration of space charge region during C-V measurement. It was recently demonstrated that introduction rate of the HDs depends linearly on proton fluence in a wide range of fluences and enhances in CZ and oxygen-rich silicon [4]. Fig. 6 demonstrates several temperature regions that are characteristic for evolution of excess donors in FZ material. One can observe rather gradual annealing of HDs from 100 to 250ºC where they reach their lowest concentration. During subsequent annealing at 300ºC, THDs appear predominantly in the region of proton end-of-range and their distribution develops towards to implanted surface. Then, the distribution of THDs starts to follow distribution of primarily radiation defects and reach maximum concentration of approximately $6 \times 10^{15}$ cm$^{-3}$ at 350ºC. Annealing at 400ºC only slightly decreases its peak without significant change of profile shape. Further annealing reduces THDs peak concentration more than two times, however, the distribution still remains localized close to projected range of protons. The evolution of excess donors dramatically changes when hydrogen plasma treatment is inserted between proton implantation and annealing procedure. Results of C-V
concentration 5×10^{15} \text{cm}^{-3} that is approximately the same as in reference sample. Further annealing at 300ºC generates THDs with peak maximum at 5.9 \mu m. Then, the profile of THDs shifts in opposite direction and significantly extends showing two maxima at 350ºC. Its right shoulder peaks at 10 \mu m that is 0.4 \mu m more deep than simulated distribution of protons. At 400ºC, the profile follows distribution of primary radiation defects and reaches the maximum donor concentration at 250ºC similarly to reference sample. However, HDs have a lower amplitude at the same time. HDs have a lower amplitude at the same time. HDs have a lower amplitude at the same time.

The decrease of concentration of HDs is more than two times in comparison with the reference sample. The similar evolution of excess donors was also monitored in CZ silicon.

As it was discussed in previous paragraph, plasma treatment introduces large amount of radiation defects on surface and into subsurface region. The results of spreading resistance measurement received on plasma treated samples subjected to proton implantation with fluence 1×10^{14} \text{cm}^{-2} and treated in rf hydrogen plasma. Reference diodes without plasma treatment are also shown for comparison.

**Influence of plasma treatment on device parameters**

Fig. 8 demonstrates reverse current of p^+nn^+ FZ and CZ diodes implanted by 700 keV proton to fluence 1×10^{14} \text{cm}^{-2} and treated in rf hydrogen plasma. Reference diodes without plasma treatment are also shown. The figure shows that the magnitude of reverse current generated in FZ and CZ diodes is approximately two times higher than in the diodes without plasma treatment. This extra leakage can be attributed to enhanced defect states formed on treated surface and subsurface region. Overall reverse current is higher in CZ diodes since, as it was discussed in previous paragraph, this substrate allows higher defect introduction rate for equivalent proton fluence. Decrease of current between 100 and 200ºC is mainly given by annealing out of VP centers. The remaining divacancies V^{<0}_2 transform to V_xO^{<0}_2 centers at approximately 225-250ºC. Higher concentration of interstitial oxygen enhances this transformation in CZ silicon. Therefore, we observe slower leakage annealing up 350ºC in CZ diodes in contrast to untreated FZ diode where the leakage sharply decreases at 300ºC. This decrease indicates annealing out of V_xO^{<0}_2 centers and occurs at temperatures higher than 400 ºC in CZ diode. According to DLTS measurement showed in Fig. 5, annealing of plasma treated sample generates new defect levels in silicon band gap. This can explains slower removing of leakage in plasma treated diodes after annealing at 400 ºC.

Table 2. compares OCVD lifetime measured on FZ silicon for interval of annealing temperatures where generation of excess THDs is the most effective. One can see that, in reference diodes, lifetime increases when annealing temperature grows. In case of sample subjected
CONCLUSIONS

The effect of plasma treatment on radiation defects introduced into silicon p+nn+ diodes by proton implantation was investigated in wide range of proton fluences. The results of DLTS measurement demonstrate that hydrogen plasma efficiently removes majority of vacancy-related defects generated by proton implantation in both FZ and CZ substrates for lower proton fluences. Both, plasma treatment and post-implantation annealing lead to appearing of new defects in silicon band gap. Some of them have high concentration even after annealing at 450°C. These defects deteriorate electrical properties of thermal hydrogen-related shallow donors (THDs) and increase diode leakage. The results of C-V measurement on plasma treated diodes showed no improvement in THDs formation in comparison with only implanted samples.

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<table>
<thead>
<tr>
<th>Samples</th>
<th>Proton fluence (cm$^{-2}$)</th>
<th>Annealing Temperature (°C)</th>
<th>OCVD lifetime (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>1×10$^{14}$</td>
<td>300</td>
<td>34</td>
</tr>
<tr>
<td>Treated by H plasma</td>
<td>3×10$^{14}$</td>
<td>350</td>
<td>40</td>
</tr>
<tr>
<td>Treated by H plasma</td>
<td>3×10$^{15}$</td>
<td>400</td>
<td>55</td>
</tr>
</tbody>
</table>

Table 2. OCVD lifetime measured on reference and plasma treated FZ diodes at temperature range 300-400°C.