

Manuscript version: Published Version

The version presented in WRAP is the published version (Version of Record).

Persistent WRAP URL:

<http://wrap.warwick.ac.uk/158723>

How to cite:

The repository item page linked to above, will contain details on accessing citation guidance from the publisher.

Copyright and reuse:

The Warwick Research Archive Portal (WRAP) makes this work by researchers of the University of Warwick available open access under the following conditions.

Copyright © and all moral rights to the version of the paper presented here belong to the individual author(s) and/or other copyright owners. To the extent reasonable and practicable the material made available in WRAP has been checked for eligibility before being made available.

Copies of full items can be used for personal research or study, educational, or not-for-profit purposes without prior permission or charge. Provided that the authors, title and full bibliographic details are credited, a hyperlink and/or URL is given for the original metadata page and the content is not changed in any way.

Publisher's statement:

Please refer to the repository item page, publisher's statement section, for further information.

For more information, please contact the WRAP Team at: wrap@warwick.ac.uk

Formation and Elimination of Electrically Active Thermally-Induced Defects in Float-Zone-Grown Silicon Crystals

Joyce Ann T. De Guzman^{1,a)}, Vladimir P. Markevich¹, Jack Mullins¹, Nicholas Grant², John D. Murphy², Daniel Hiller³, Matthew P. Halsall¹, and Anthony R. Peaker¹

¹*Photon Science Institute and Department of EEE, University of Manchester, M13 9PL, UK*

²*School of Engineering, University of Warwick, Coventry, CV4 7AL, UK*

³*Chair of Nanoelectronics, Institute of Semiconductors and Microsystems (IHM),
Technische Universität Dresden, 01062 Dresden, Germany*

^{a)}Corresponding author: joyceann.deguzman@manchester.ac.uk

Abstract. Understanding the origins of the phenomena that limit the minority carrier lifetime in float-zone-grown silicon (FZ-Si) is an important area in photovoltaics research. Although FZ silicon has been applauded for its stability, purity, and high minority carrier lifetime, it has been found recently that severe degradation of the minority carrier lifetime occurs in FZ-Si crystals upon thermal treatments in the temperature range 400-700 °C and upon light soaking at elevated (~100 °C) temperatures. In this work, deep level transient spectroscopy (DLTS) and high-resolution Laplace DLTS have been used to elucidate the formation and elimination processes of the electrically active thermally-induced defects. Float-zone-grown n-type Si crystals with and without added nitrogen from different suppliers have been studied. It has been found that the spectra of deep levels from thermally-induced defects are different in FZ-Si crystals from different manufacturers. Significant qualitative changes were observed in the DLTS spectra after heat-treatments of the FZ-Si samples at different temperatures for different treatment duration. These results indicate various defect reactions occurring upon heat-treatments in FZ-Si materials with varying ensembles of intrinsic defects, doping, and residual impurities in the as-grown state. Also, we have found that hydrogenation from a remote plasma source with subsequent low-temperature annealing has resulted in the total deactivation of thermally-induced defects in FZ silicon.

INTRODUCTION

Due to its extremely high purity and low defect concentrations (particularly low concentrations of oxygen-related defects), float-zone-grown silicon (FZ-Si) has significant potential as a material for high-efficiency solar cells.¹ However, it has been found recently that severe degradation of the minority carrier lifetime occurs in FZ-Si crystals upon thermal treatments in the temperature range 400-700 °C²⁻⁶ and upon light soaking at slightly elevated (~100 °C) temperatures.⁷⁻⁹ Previously, a number of unidentified deep level states have been detected by means of deep level transient spectroscopy (DLTS) and minority carrier transient spectroscopy (MCTS) in FZ-Si samples, which have been subjected to heat-treatments in the temperature range from 400 to 700 °C.³⁻⁶ It has been argued that light impurities, particularly nitrogen and growth-related vacancy complexes could be linked to the introduction of lifetime limiting defects upon annealing.²⁻⁶

Nitrogen is usually incorporated into the silicon melt during growth for the enhancement of crystal strength and mechanical stability as well as to avoid the accumulation of silicon vacancies into voids, thereby improving the quality of the wafers.¹⁰⁻¹² Normally, most FZ silicon manufacturers use a relatively fast growth rate that typically results in the appearance of excess vacancies in the central region of the ingots.^{13,14} These vacancies can agglomerate into clusters of different sizes or interact with other impurities to form complexes of defects. Note that vacancies could

also be introduced by dislodging silicon atoms in the lattice during processing steps such as plasma treatment, wet chemical etching, sputtering, and dielectric deposition, among others.¹⁵

Hydrogen has been established to be a passivating agent for electrically active defects in silicon.¹⁶ It has been found that hydrogen enhances the mitigation or deactivation of boron-oxygen defects responsible for the light-induced degradation (LID) in CZ-grown Si solar cells and can passivate detrimental transition metal impurities and dislocation clusters.¹⁷⁻²² Further, it has been demonstrated in some studies that hydrogenation improves the lifetime of minority carriers in Si crystals grown by float-zone technique (FZ-Si).^{6,23,24} Hydrogen atoms are found to be very effective in the passivation of dangling bonds associated with vacancy-related complexes.²⁵ A single Si vacancy can bond up to 4 hydrogen atoms (VH_n ; $n=1,2,3,4$) forming vacancy-hydrogen complexes.¹⁵

Recently, a bulk lifetime degradation due to the activation of recombination active thermally-induced defects has been reported to occur in n-type FZ silicon slices that have been subjected to heat-treatments in the temperature range 300-800 °C with the use of different annealing techniques such as rapid-thermal annealing (RTA), tube furnace annealing (TFA), and flash lamp annealing.⁶ It has been shown in the study that the recovery of the degraded lifetime in FZ silicon is attainable by furnace annealing at 900 °C for 60 min, while hydrogenation of the samples from the deposited silicon nitride (SiN_x) layers has been only partially successful for the elimination of the detrimental thermally-activated defects. It has been demonstrated that in FZ silicon wafers covered with hydrogen-rich SiN_x dielectric layers, a partial recovery of the degraded bulk lifetime occurs upon heat-treatments in the temperature range 400-700 °C. Furthermore, it has been found that the hydrogenation-induced improvement in the lifetime is not very stable since heat-treatments of the annealed hydrogenated slices after removal of the dielectric layers have again resulted in severe lifetime degradation.⁶ Following these recent findings, we have examined the impact of hydrogen-plasma treatments with the following low temperature (100-400 °C) annealing on the electrically active thermally-induced defects in n-type FZ-Si, which were subjected to rapid-thermal annealing and tube furnace annealing treatments, similar to those carried out in Ref. [6].

In this work, the thermally-induced deep level traps have been characterized with the use of junction capacitance-based techniques in n-type FZ-Si materials from different growers. Impacts of growth and heat-treatments conditions on the formation and elimination of the thermally-induced defects have been studied. Special experiments have been designed to investigate the involvement of grown-in vacancy-related defects, nitrogen, and hydrogen atoms in the formation and disappearance of the thermally-induced defects.

EXPERIMENTAL DETAILS

Samples for this study have been prepared from several sets of n-type float-zone-grown wafers from three different suppliers. All the wafers were 100 mm in diameter with a thickness between 260 and 500 μm . The resistivity of the wafers was in the range between 1 and 2.5 $\Omega\text{-cm}$, except one set, the resistivity of which was 100 $\Omega\text{-cm}$. Nitrogen-rich and nitrogen-lean wafers have been selected and specified. Quarters of these wafers were subjected to RCA cleaning and then to heat-treatments in different gas ambient (oxygen, argon, and nitrogen) for different durations at temperatures in the range 400–1000 °C. For some specific heat-treatments with varying temperature or duration of annealing and the following DLTS measurements, smaller samples with dimensions of about 10 × 15 mm² were cut from the central part of the same 4-inch wafer. Before cutting small samples for these specific heat-treatment experiments, we carried out minority carrier lifetime measurements on the as-received wafer using SemiLab WT-2000PVN lifetime mapper and iodine/ethanol surface passivation and cut the samples from the regions with similar lifetimes.

Photoluminescence (PL) imaging carrier lifetime measurements were carried out on nitrogen-rich and nitrogen-lean wafers in the as-grown state and after annealing at 600 °C for 30 min in oxygen (degraded state). Superacid-based surface passivation technique was undertaken as it provides excellent surface recombination velocities around 1 cm/s.^{26,27} PL images were used in identifying regions with low lifetime and samples from these regions were cut for electrical measurements.

One set of samples underwent RTA in O₂ gas ambient at 550 °C to investigate the activation of deep level defects in FZ-Si wafers upon RTA at different time duration (timescale of seconds). Complete details of the RTA processing can be found in Ref. [6].

To study interactions of hydrogen with thermally-induced defects, some slices were subjected to hydrogenation treatments in remote radio-frequency hydrogen plasma with subsequent low-temperature annealing to diffuse hydrogen further to the bulk. For the hydrogen-plasma treatment, samples underwent a 60-min treatment at 295 K using the following plasma parameters: RF power at 50 W with 1-2 mbar chamber pressure and 200-250 cc/min gas

flow. After the hydrogenation process, isochronal annealing at low-temperature in the range 100-400 °C for 30 mins were carried out to investigate the effects of the diffusion of the hydrogen towards the bulk.

In order to establish the possible role and existence of vacancies, nickel was intentionally in-diffused into samples of nitrogen-rich and nitrogen-lean float zone silicon. This process provides an indication of vacancy concentration within the silicon wafers by measuring the concentration of electrically active nickel atoms at the sites of silicon lattice.^{5,28} Thermal evaporation of nickel on the surface of nitrogen-lean and nitrogen-rich samples was carried out followed by annealing at 500 °C for 90 min. Prior to electrical measurements, etching in a mixture of hydrofluoric acid and nitric acid (1HF:7HNO₃) was carried out to remove the evaporated nickel.

Circular Schottky barrier diodes (SBDs) of diameter 1 mm were formed on the surface of the samples using thermal evaporation of Au through a shadow mask for n-type samples. Ohmic contacts were fabricated by thermal evaporation of aluminium at the back surface of the sample. No post-deposition annealing was carried out. The diodes were characterized using capacitance-voltage and current-voltage measurements, and the highest quality diodes were chosen for DLTS and high-resolution L-DLTS measurements.^{29,30}

EXPERIMENTAL RESULTS AND DISCUSSION

Effects of Growth Conditions on the Formation of Electrically Active Defects upon Heat-treatments of FZ-Si Crystals

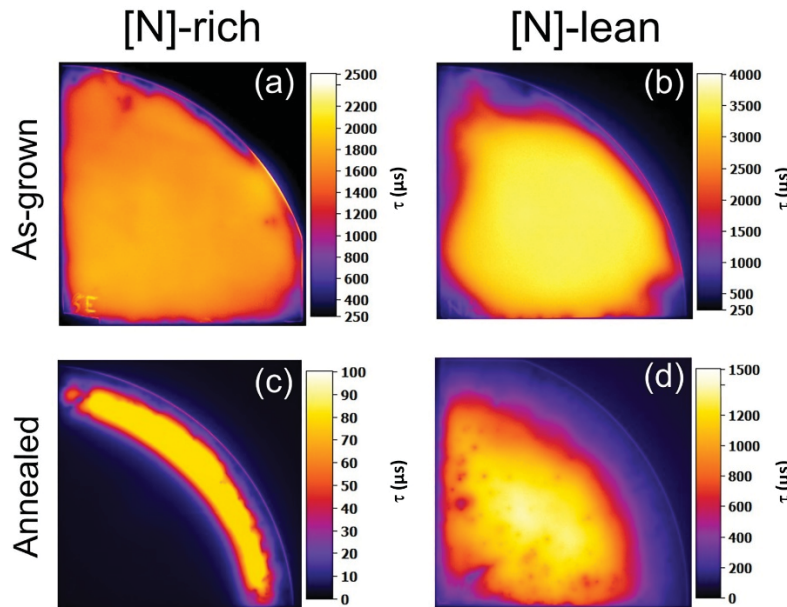


FIGURE 1. Calibrated photoluminescence carrier lifetime images of quarters of 100 mm wafers of nitrogen-rich (a&c) and nitrogen-lean (b&d) n-type FZ silicon in as-grown and annealed state. Lifetime degradation is more severe in the annealed nitrogen-rich FZ wafers after annealing. Effective lifetime values (τ) are expressed in microseconds (μs) and injection conditions are described in the text.⁵ J. Mullins et al., *J. Appl. Phys.* **124**, 035701, 2018; licensed under a Creative Commons Attributions (CC-BY) license.

As mentioned in the Introduction, the results available in the literature indicate that the recombination active defects induced by thermal treatments are preferentially formed in the vacancy-rich regions of FZ-Si wafers.²⁻⁶ Further, more severe degradation of minority carrier lifetime was detected in nitrogen-rich FZ-Si compared to that in the nitrogen-lean FZ-Si wafers.^{3,5} Results of the present work are consistent with the previous findings. Figure 1 compares calibrated PL minority carrier lifetime images of nitrogen-rich and nitrogen-lean FZ-Si slices before and after a heat-treatment at 600 °C for 30 min in an oxygen gas ambient. Due to the large lifetime variations between samples, PL imaging measurements were carried out with different exposure conditions. As-grown samples in Fig. 1 (a) and (b) were measured with a photon flux of $1.2 \times 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$ and an exposure time of 0.1 s. This resulted in excess carrier densities typically in the range 2 to $8 \times 10^{15} \text{ cm}^{-3}$. Moreover, the sample in Fig. 1 (c) was measured with a photon flux

of $4.2 \times 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$ and an exposure time of 0.5 s. The low lifetime region had an excess carrier density of around $5 \times 10^{13} \text{ cm}^{-3}$ and the high lifetime region had an excess carrier density of approximately $1 \times 10^{15} \text{ cm}^{-3}$. The sample in Fig. 1 (d) was measured with a photon flux of $3.0 \times 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$ for 0.3 s. This has resulted in an excess carrier density of approximately $1 \times 10^{16} \text{ cm}^{-3}$ in the high lifetime region and around 1 to $4 \times 10^{15} \text{ cm}^{-3}$ in the lower lifetime edge region.

The lifetime measurements have shown a substantial heat-treatment-induced decrease in the measured effective minority carrier lifetime of the nitrogen-rich wafer, while a much less pronounced reduction in the lifetime of the nitrogen-lean sample has been detected. It can be seen in Fig. 1 (c) the non-uniform distribution of lifetime with a ring-like pattern at the center of the wafer after annealing of the nitrogen-rich FZ-Si sample. This severe reduction in the lifetime at the central region of the nitrogen-rich wafer has been argued to be related to vacancy reactions.⁵ The high pulling rate is thought to result in the formation of excess vacancies in central parts of the growing ingots.^{13,14}

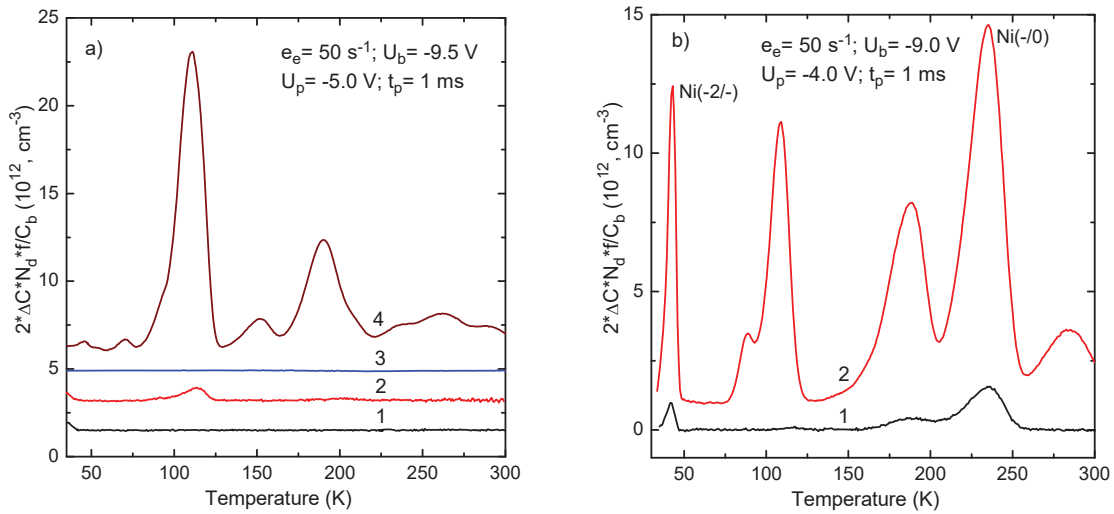


FIGURE 2. a) DLTS spectra recorded on Schottky diodes on slices from the central part of n-type FZ-Si wafers: (1 and 2) nitrogen-lean with resistivity of $1.5 \Omega\text{-cm}$ and (3 and 4) nitrogen-rich with resistivity of $2.5 \Omega\text{-cm}$. Spectra 1 and 3 were recorded on diodes on as-grown slices. Spectra 2 and 4 were recorded on diodes on the slices which were subjected to a heat-treatment at $500 \text{ }^\circ\text{C}$ for 30 min in an Ar gas ambient. b) DLTS spectra recorded on Schottky diodes on slices from the central parts of n-type FZ-Si wafers: (1) nitrogen-lean and (2) nitrogen-rich. Both slices were subjected to a 90 min heat-treatment at $500 \text{ }^\circ\text{C}$ in an N_2 ambient with Ni films deposited on both surfaces. Measurement settings are shown in the graphs: DLTS rate window (e_e), bias voltage (U_b), filling pulse voltage (U_p), and filling pulse length (t_p). On the Y-axis concentration values $Y = 2 \times (\Delta C / C_b) \times N_d \times f$ are plotted, where ΔC is the magnitude of a capacitance transient, C_b is the bias capacitance, and f is the correction function, which takes into account depletion widths at the bias and pulse voltages.^{28,30} The Y values at the peak maxima are close to the corresponding trap concentrations. The spectra are shifted along the vertical axis for clarity.

Figure 2 (a) compares conventional DLTS spectra recorded on samples from central parts of nitrogen-rich and nitrogen-lean wafers from the same supplier before and after annealing at $500 \text{ }^\circ\text{C}$ for 30 min in an argon gas ambient. Electron traps with concentrations in the range from $1 \times 10^{12} - 2 \times 10^{13} \text{ cm}^{-3}$ are detected in the spectrum of the heat-treated nitrogen-rich sample, while the concentrations of deep level electronic traps in the heat-treated nitrogen-lean sample were negligible. These results indicate that nitrogen introduced into FZ-Si crystals during growth plays a vital role in the formation of thermally-activated defects in n-type FZ-grown silicon.^{3,5,6} It is not clear, however, if nitrogen is directly involved in the defect structures or its primary role is in the suppression of formation of vacancy clusters during growth of FZ-Si ingots.

We have tried to detect vacancy-related defects in as-grown and heat-treated N-rich and N-lean FZ-Si samples using positron annihilation spectroscopy (PAS). Unfortunately, the PAS measurements were unsuccessful, as the PAS technique does not have sufficient detectivity to examine the low concentration of vacancy-related defects in our FZ-Si materials. Consequently, we have used another technique, in-diffusion of Ni, to detect the presence of vacancies in the FZ-Si materials.²⁸ The interaction of in-diffused interstitial Ni atoms with vacancies results in the stabilization of Ni atoms at substitutional lattice sites. The Ni_i atoms introduce three energy levels into the band gap,^{28,32} which can be easily detected by DLTS. Figure 2 (b) compares the DLTS spectra on samples from central parts of nitrogen-rich

and nitrogen-lean wafers from the same supplier, which were subjected to a Ni in-diffusion treatment. The DLTS peaks with their maxima at 43 K and 235 K in the spectra are related to the second and first acceptor levels of N_i . It is clear from a comparison of the spectra that the ingot growth in nitrogen ambient resulted in a much higher concentration ($> 1 \times 10^{13} \text{ cm}^{-3}$) of available vacancies in this ingot compared to that in the ingot grown in the ambient without nitrogen ($< 2 \times 10^{12} \text{ cm}^{-3}$). This observation confirms the suggested effect of nitrogen in suppressing agglomeration of vacancies into stable extended defects (voids) during float-zone growth of silicon.^{1,12}

We have further compared the DLTS spectra for the heat-treated slices from nitrogen-rich n-type FZ-Si slices from different suppliers. Figure 3 shows DLTS spectra recorded on n-type N-rich FZ-Si samples from three suppliers, which were subjected to a 500 °C heat-treatment for 30 min in an Ar ambient. More than ten signals related to electron emission from deep-level defects are detected in the spectra. The “emission signatures” of these signals, activation energies for electron emission and pre-exponential factors or apparent capture cross-sections, have been reported in Refs [3] and [5]. Notably, the deep level spectra of thermally-induced defects are different in FZ-Si crystals from different growers. It can be observed that some of the DLTS peaks present in a wafer from one supplier are not visible in the samples supplied by another grower.

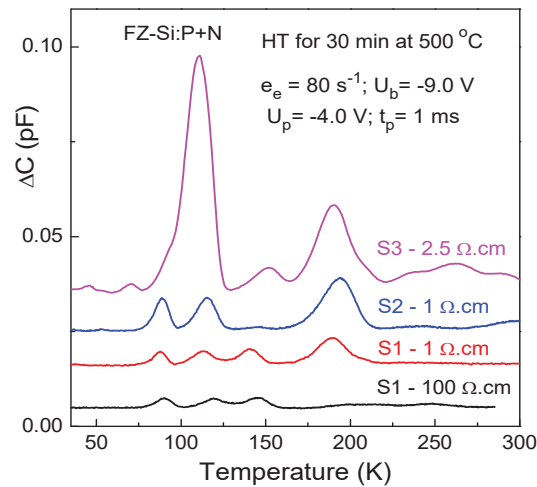


FIGURE 3. DLTS spectra of samples from N-rich n-type FZ-Si wafers from different suppliers, which were subjected to 30-min heat-treatment at 500 °C in an Ar gas ambient. Measurement settings are shown in the graph. The spectra are shifted along the vertical axis for clarity.

The results presented above and those available in the literature indicate that the defect reactions, which occur in FZ-Si wafers upon annealing and result in the appearance of recombination active deep-level defects, depend on defect-impurity ensemble in the as-grown wafers. Clear evidence for the involvement of Si lattice vacancies and nitrogen impurity atoms in the formation of the thermally-induced deep level defects have been found.^{3,5,6} It can also be speculated that oxygen and carbon impurity atoms are involved in some defect reactions. Concentrations of these impurities are not high in FZ-Si crystals compared to those in Czochralski-grown Si but can be in the range of 10^{15} - 10^{16} cm^{-3} , which is comparable or even higher than concentrations of vacancy-related defects and nitrogen. The possible involvement of carbon in the thermally-induced defect reactions in FZ-Si crystals has been mentioned and discussed recently in Ref. [33].

Effects of Heat-treatment Conditions on the Formation of Electrically Active Defects upon Heat-treatments of FZ-Si Crystals

It is clear from the results available in the literature that heat-treatment conditions influence the introduction rates of the recombination active thermally-induced defects in FZ-Si crystals.^{3,6} The effects of heat-treatment temperature and duration on changes in minority lifetime in different FZ-Si crystals have been clearly observed and discussed.^{3,6} We will further discuss these effects below.

In the majority of the reported investigations, the samples were heat-treated without dielectric films deposited on them. The effect of annealing ambient (either oxygen, nitrogen, or argon gases) on the formation of thermally induced defects was studied in Ref. [5] by means of DLTS. It was found that the annealing ambient had only a marginal effect on the introduction of electrically active defects upon heat-treatments of slices from N-rich FZ-Si wafers. This result is expectable if one takes into account the facts that i) the thermally induced defects are formed in the bulk areas of the samples and ii) in-diffusion lengths for O, N, and Ar impurities into silicon are rather short upon the heat-treatments that result in the effective formation of the thermally induced defects. It has been recently reported that there are some differences in the changes of minority carrier lifetime for the samples which have been heat-treated at temperatures of the effective formation of the thermally induced defect either with or without SiN_x dielectric films on the surface.^{6,34} It has been speculated that some of the observed effects can be related to hydrogen in-diffusion into the samples from the deposited dielectric layers.^{6,34} However, further studies are necessary to elucidate the origin of the observed effects upon heat-treatments of FZ-Si slices with the deposited dielectric films as the stress at the dielectric-Si interface alters the intrinsic defect concentrations.

No systematic results have been reported in the available literature on the changes in the spectra of deep level defects upon changes in the temperature and duration of heat-treatments of FZ-Si wafers. Figure 4 shows DLTS spectra recorded on samples from nitrogen-rich FZ-Si:P wafers, which were subjected to 30 min heat-treatments in the temperature range from 400 °C to 900 °C in an Ar gas ambient and to isothermal annealing at 500 °C. No electrically active traps were detected in the as-grown FZ-Si sample. Heat-treatments in the 400-700 °C temperature range have resulted in the introduction of several deep level traps with concentrations of some defects in the range of 10^{12} - 10^{13} cm^{-3} . An important observation is that there are significant qualitative changes in the spectra recorded after the 30-min treatments at different temperatures or after the treatments of different duration at 500 °C. It appears that some multiple defect reactions occur depending on the heat-treatment temperature and duration. Annealing at higher temperatures above 800 °C, has not resulted in the introduction of electronic traps. Similar results have been found in Refs [4] and [6], wherein it was reported that annealing at 1000 °C resulted in the annihilation of the defects and exhaustion of nitrogen concentration as detected by secondary ion mass spectrometry (SIMS).^{4,6}

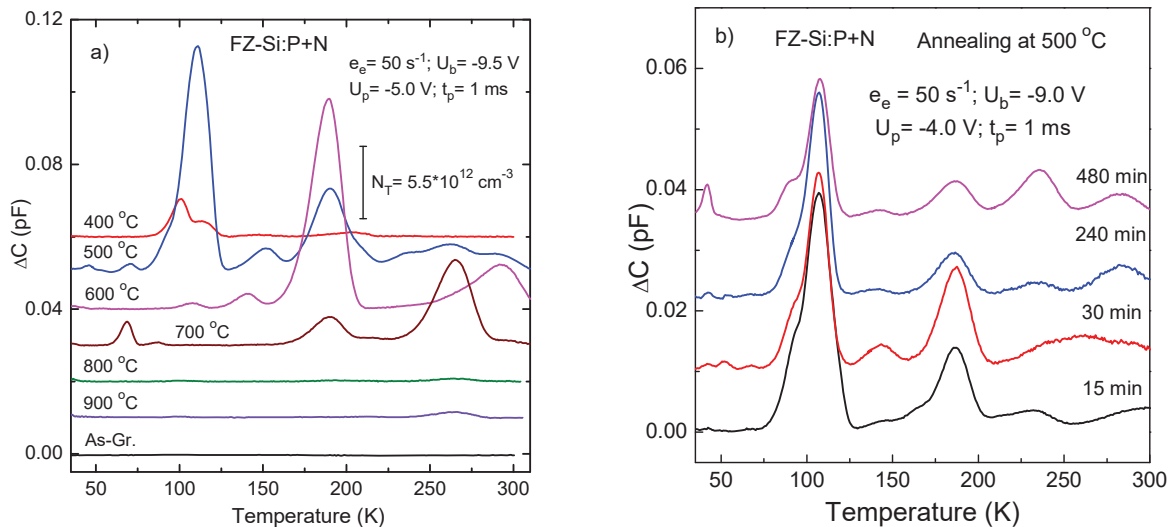


FIGURE 4. DLTS spectra of samples from n-type nitrogen-rich FZ-Si wafers with the resistivity of 2.5 $\Omega\text{-cm}$, which were subjected to a) 30 min isochronal annealing and b) thermal annealing at 500 °C for different duration. Measurement settings are shown in the graph [DLTS rate window (e_e), bias voltage (U_b), filling pulse voltage (U_p), and filling pulse length (t_p)]. The trap concentration (N_T) is shown in (a) as a unit bar. The spectra are shifted along the vertical axis for clarity.

In the majority of papers available in literature bulk lifetime degradation due to the activation of thermally-induced defects was reported after annealing in tube furnaces on the time scale of minutes or hours.²⁻⁵ Recently it has been reported to also occur in n-type FZ silicon slices that have been subjected to heat-treatments in the temperature range 400-800 °C with rapid-thermal annealing (RTA) of several seconds and flash lamp annealing of 20 ms.⁶ It is surprising how rapid and dramatic this degradation is. An RTA treatment with a dwell time of one second at 550 °C reduces the

lifetime in the core region of nitrogen-doped FZ material from a few milliseconds to 30 μ s. Possible reasons for the enhanced formation of the thermally-induced recombination active defects upon the RTA treatments have been discussed in Ref. 6. Figure 5 shows the DLTS spectra recorded on samples that underwent rapid thermal annealing at 550 °C for 1 s, 10 s, and 90 s. It can be seen that thermally-induced defects are already observable in FZ samples subjected to RTA for 1 s. It should be highlighted that the activation of these deep-level defects in nitrogen-rich FZ-samples occurs after short annealing treatment on a sub-second timescale. This observation is consistent with the findings in Ref. [6]. We have observed six electron traps in the FZ samples subjected to RTA for 1 s, 10 s, 90 s. These DLTS emission signals are similar to those due to the detected defect traps in FZ silicon subjected to conventional furnace heat-treatments as reported in the previous studies.^{3,6,24}

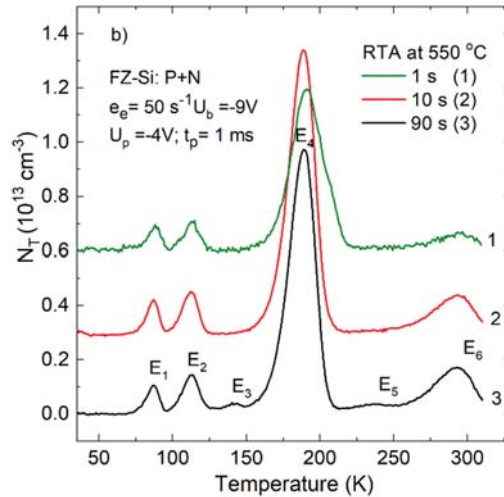


FIGURE 5. DLTS spectra of samples from n-type nitrogen-rich FZ-Si wafers with 2 Ω -cm resistivity, which were subjected to rapid thermal annealing at 550 °C for different durations. Measurement settings are shown in the graph. The spectra are shifted along the vertical axis for clarity.

Passivation of Electrically Active Thermally-induced Defects with Hydrogen in FZ-Si Crystals

It is well accepted in the solar community that hydrogen can passivate electrically active defects in silicon. The passivation effects of hydrogen differ depending on the method of hydrogen incorporation into the silicon wafers, either from the silicon nitride (SiN_x) dielectric layer (serves as anti-reflecting coatings and surface passivation layer for silicon solar cells) or via remote plasma treatments. Hydrogen atoms are mobile in silicon at room temperature and prone to interact with intrinsic defects and other impurities under favorable charge conditions.^{16,35,36} In the study by Hiller *et al.*, it has been demonstrated that in FZ silicon slices covered with hydrogen-rich silicon SiN_x passivation layers, a partial recovery of the degraded bulk lifetime occurs upon heat-treatments in the temperature range 400-800 °C. This finding indicates that the recombination centers were partially passivated due to the hydrogen-rich SiN_x layer. It has been suggested that the amount of hydrogen in-diffused into the bulk regions from the dielectric layer is not enough to passivate the electrically active defects fully.⁶ It has been further found that the hydrogenation-induced improvement of the lifetime is unstable since heat treatments of the annealed hydrogenated slices after removal of the dielectric layers have again resulted in severe lifetime degradation.

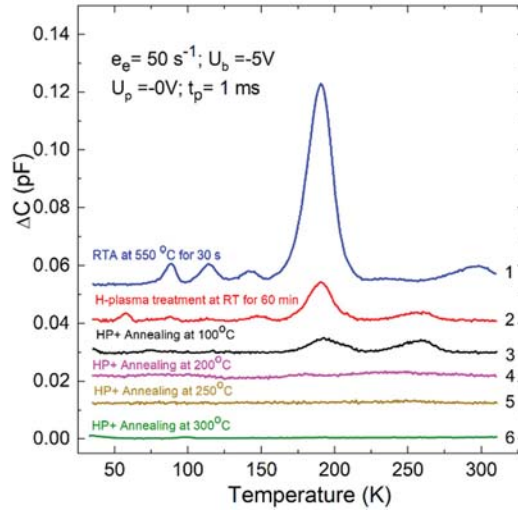


FIGURE 6. DLTS spectra recorded on samples from nitrogen-rich n-type FZ-Si wafers with 2 Ω -cm resistivity which were all subjected to RTA annealing at 550 $^{\circ}$ C for 30 s and then to the following treatments: 1) no further treatment; 2) hydrogen-plasma treatment at room temperature for 60 min; and 3-6) H-plasma treatment and subsequent isochronal annealing without bias for 30 min at 100 $^{\circ}$ C (3); 200 $^{\circ}$ C (4); 250 $^{\circ}$ C (5); 300 $^{\circ}$ C (6). The spectra are shifted along the vertical axis for clarity.

We have introduced hydrogen from a remote H plasma source into FZ-Si samples which have been subjected to treatments of different durations at 550 $^{\circ}$ C either with RTA technique or by conventional furnace annealing. The hydrogenated samples were subjected to heat treatments in the temperature range of 100-400 $^{\circ}$ C to move the introduced hydrogen deeper into the bulk regions. Figure 6 shows that after hydrogen-plasma treatment, a reduction in the concentration of all the thermally induced electron traps occurred. Further, no defect traps have been detected in the DLTS spectra of the samples subjected to hydrogenation and subsequent annealing at 200 $^{\circ}$ C, 250 $^{\circ}$ C, and 300 $^{\circ}$ C. A total elimination of recombination activity of defects with deep energy levels was observed upon annealing in the temperature range 200-300 $^{\circ}$ C. This indicates that hydrogenation and annealing can result in complete passivation of the thermally-activated defects in n-type float zone Si which were previously detectable by DLTS.

CONCLUSIONS

Lifetime degradation is more pronounced in nitrogen-rich FZ silicon than in nitrogen-lean samples indicating that the presence of nitrogen is one of the main factors that limits the lifetime of heat-treated FZ-grown silicon wafers. In general, the obtained results show that the crystal growth and heat-treatments conditions significantly impact the formation and elimination of the thermally-induced defects in FZ-Si wafers. It has been shown that multiple defect reactions occur in FZ-Si crystals upon heat-treatments, which result in the formation of several defects with deep energy levels. It is found that the defects are preferentially formed in the vacancy-rich regions of the wafers. The introduction of hydrogen has been found to result in strong passivation of all the thermally induced deep level traps in n-type FZ-silicon. Therefore, it is suggested that vacancy-related defects can be passivated by mobile hydrogen atoms in silicon upon hydrogen-plasma treatment followed by low-temperature annealing in the range 200-300 $^{\circ}$ C.

ACKNOWLEDGMENTS

We would like to thank EPSRC (UK) for funding this work via grant EP/TO25131/1. J.A.T. De Guzman would like to thank the Government of the Philippines through the Department of Science and Technology (DOST) for her PhD funding. D. Hiller would like to thank the Alexander von Humboldt Foundation for a Feodor Lynen Fellowship and Return Fellowship. Work at the University of Warwick was supported by EPSRC via grants EP/J01768X/2 and EP/M024911/1. Requests for data related to this publication should be made to the corresponding author.

REFERENCES

1. W. von Ammon, *Phys. Status Solidi A* 211, 2461-2470 (2014).
2. N. E. Grant, F. Rougieux, and D. Macdonald, *Sol. State Phen.* 242, 120–125 (2016).
3. N. E. Grant, V.P. Markevich, J. Mullins, A.R. Peaker, F. Rougieux, and D. Macdonald, *Phys. Status Solidi RRL* 10, 443–447 (2016).
4. N. E. Grant, V.P. Markevich, J. Mullins, A.R. Peaker, F. Rougieux, D. Macdonald, and J.D. Murphy, *Phys. Status Solidi A* 213, 2844-2849 (2016).
5. J. Mullins, V.P. Markevich, M. Vaqueiro-Contreras, N.E. Grant, L. Jensen, J. Jablonski, J.D. Murphy, M.P. Halsall, and A.R. Peaker, *J. Appl. Phys.* 124, 035701 (2018).
6. D. Hiller, V.P. Markevich, J.A.T. De Guzman, D. Konig, S. Prucnal, W. Bock, J. Julin, A.R. Peaker, D. Macdonald, N. E. Grant, & J.D. Murphy, *Phys. Status Solidi A* 217, 2000436 (2020).
7. T. Niewelt, M. Selinger, N. E. Grant, W. Kwapił, J. D. Murphy, and M. C. Schubert, *J. Appl. Phys.* 121, 185702 (2017).
8. D. Sperber, A. Herguth, and G. Hahn, *Phys. Status Solidi RRL* 11, 1600408 (2017).
9. B. Hammann, J. Engelhardt, D. Sperber, A. Herguth, and G. Hahn, *IEEE J. Photovoltaics* 10, 85-93 (2020).
10. K. Sumino, I. Yonenaga, M. Imai, and T. Abe, *J. Appl. Phys.* 54, 5016-5020 (1983).
11. C. R. Alpass, J. D. Murphy, R. J. Falster, and P. R. Wilshaw, *J. Appl. Phys.* 105, 013519 (2009).
12. H. Kageshima, A. Taguchi, and K. Wada, *Appl. Phys. Lett.* 76, 3718-3720 (2000).
13. T. Abe, *J. Crystal Growth* 334, 4-15 (2011).
14. T. Abe and T. Takahashi, *J. Crystal Growth* 334, 16-36 (2011).
15. M. A. Roberson, and S. K. Estreicher, *Phys. Rev. B* 49, 17040-17049 (1994).
16. A.R. Peaker, V. P. Markevich, and L. Dobaczewski, in *Defects in Microelectronic Materials and Devices*, ed. by D.M. Fleetwood, S.T. Pantelides, and R.D. Schrimpf, pp. 27-56 (CRC Press, Boca Raton, 2009).
17. G. Hahn, M. Käs, and B. Herzog, *Sol. State Phen.* 156-158, 343-349 (2010).
18. S. Wilking, A. Herguth, and G. Hahn, *J. Appl. Phys.* 113, 194503 (2013).
19. B.J. Hallam, P.G. Hammer, S.R. Wenham, M.D. Abbott, A. Sugianto, A.M. Wenham, C.E. Chan, G.Q. Xu, J. Kraiem, J. Degoulange, and R. Einhaus, *IEEE J. Photovoltaics* 4, 88-95 (2014).
20. B. Hallam, M. Abbott, N. Nampalli, P. Hammer, and S. Wenham, *J. Appl. Phys.* 119, 065701-(1-9) (2016).
21. D. C. Walter and J. Schmidt, *Sol. Energy Mater. Sol. Cells* 158, 91-97 (2016).
22. J. Mullins, S. Leonard, V.P. Markevich, I.D. Hawkins, P. Santos, J. Coutinho, A.G. Marinopoulos, J.D. Murphy, M.P. Halsall, and A.R. Peaker, *Phys. Status Solidi A* 214, 1700304 (2017).
23. F.E. Rougieux, N.E. Grant, C. Barugkin, D. Macdonald, and J.D. Murphy, *IEEE J. Photovoltaics* 5, 495-498 (2015).
24. Y. Zhu, F. Rougieux, N. Grant, J.A.T. de Guzman, J.D. Murphy, V.P. Markevich, G. Coletti, A.R. Peaker, and Z. Hameiri, *IEEE J. Photovoltaics* 11, 26-35 (2020).
25. R. Jones, B.J. Coomer, J.P. Goss, B. Horahine, and A. Resende, *Sol. State Phen.* 71, 173-248 (2000).
26. N.E. Grant, T. Niewelt, N.R. Wilson, E.C. Wheeler-Jones, J. Bullock, M. Al-Amin, M.C. Schubert, A.C. van Veen, A. Javey, and J.D. Murphy, *IEEE J. Photovoltaics* 7, 1574-1583 (2017).
27. A.I. Pointon, N.E. Grant, E.C. Wheeler-Jones, P.P. Altermatt, and J.D. Murphy, *Sol. Energy Mater. Sol. Cells* 183, 164-172 (2018).
28. M. A. Khorosheva, V. I. Orlov, N. V. Abrosimov, and V. V. Kveder, *J. Exp. Theor. Phys.* 110, 769-774 (2010).
29. A.R. Peaker, V.P. Markevich, and J. Coutinho, *J. Appl. Phys.* 123, 161559 (2018).
30. L. Dobaczewski, A.R. Peaker, and K. Blonde Nielsen, *J. Appl. Phys.* 96, 4689-4728 (2004).
31. D. Stievenard and D. Vuillaume, *J. Appl. Phys.* 60, 973-979 (1986).
32. L. Scheffler, V.I. Kolkovskiy, and J. Weber, *J. Appl. Phys.* 116, 173704 (2014).
33. J.A.T. de Guzman, V.P. Markevich, D. Hiller, I.D. Hawkins, M.P. Halsall, and A.R. Peaker, *J. Phys. D.: Appl. Phys.*, <https://doi.org/10.1088/1361-6463/abf807> (2021).
34. Y. Zhu, F. Rougieux, N. Grant, J. Mullins, J.A. De Guzman, J.D. Murphy, V. P. Markevich, G. Coletti, A.R. Peaker, and Z. Hameiri, *AIP. Conf. Proc.* 2147, 140014 (2019).
35. B.J. Hallam, P.G. Hammer, A.M. Ciesla née Wenham, C.E. Chan, B. Vicari Stefani, and S. Wenham, *Prog. Photovoltaics Res. Appl.* 28, 1217 -1238 (2020).
36. B. Sopori, Y. Zhang, and N.M. Ravindra, *J. Electron. Mater.* 30, 1616-1627 (2001).