Influence of Annealing and Bulk Hydrogenation on Lifetime-Limiting Defects in Nitrogen-Doped Floating Zone Silicon

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***Abstract*—A recombination active defect is found in as-grown high-purity floating zone n-type silicon wafers containing grown-in nitrogen. In order to identify the properties of the defect, injection-dependent minority carrier lifetime measurements, secondary ion mass spectroscopy measurements, and photoluminescence lifetime imaging are performed. The lateral recombination center distribution varies greatly in a radially symmetric way, while the nitrogen concentration remains constant. The defect is shown to be deactivated through high temperature annealing and hydrogenation. We suggest that a nitrogen-intrinsic point defect complex may be responsible for the observed recombination.**

***Index Terms*—Floating zone, minority carrier lifetime, nitrogen, silicon.**

I. Introduction

The presence of interstitial oxygen has been shown to negatively affect the minority carrier lifetime in silicon devices either through the boron–oxygen defect [2], [3], thermal donors [4], [5], other grown-in defects [6] or as a consequence of high temperature processing [7]–[11]. Hence, there is a growing interest in the photovoltaic community in using oxygen-lean growth methods, such as the floating-zone (FZ) method to produce wafers for high-efficiency silicon solar cells. However, relatively high concentrations of nitrogen are commonly measured in silicon grown from the FZ method with typical nitrogen concentrations above 1×10^{14} cm^{-3} and up to the solubility of $\sim 4.5 \times 10^{15}$ cm^{-3} from the atmosphere in which the crystals are grown [12]. Nitrogen is well known to mitigate the impact of extended defects [13]–[15]. For instance, it effectively suppresses the formation of vacancy and interstitial aggregates in FZ crystals [13], [14] (by reacting with vacancies and silicon interstitials via the reactions $N_2 + V \rightarrow N_2V$ and $N_2V + I \rightarrow N_2$) [16]. Nitrogen also pins dislocations [15], thus improving mechanical stability at high temperatures. Despite its many benefits, nitrogen also forms electrically active defects situated near the conduction band in FZ silicon [17]. Upon subsequent annealing, these defects disappear and deeper defects are created [17]–[21]. The carrier lifetime (and hence solar cell efficiency) will potentially be affected by the presence of nitrogen-related defects. Unfortunately, very little data regarding the influence of nitrogen-related defects on the minority carrier lifetime have been published to date [22].

In this paper, we measure the minority carrier lifetime in nitrogen-doped FZ silicon and nitrogen-lean Cz silicon. While the lifetime is initially lower in the nitrogen-doped wafers, we show that it improves after high temperature annealing to values similar to the nitrogen-lean wafers. Through photoluminescence (PL) imaging, we show that the defect distribution may be related to the vacancy distribution because of the radial symmetry observed. Finally, we demonstrate that the defect(s) can be partially hydrogenated using a hydrogen rich silicon nitride.

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II. Experimental Methods

The samples used in this study were cut from two 100-mm diameter phosphorus-doped n-type silicon ingots. The first wafer of resistivity 1.5 Ω·cm and thickness 250 μm was from a control Cz ingot with no or very low nitrogen concentration. Three other wafers of resistivity 1.5 Ω·cm and thickness 215 μm were from a FZ ingot grown under both argon and nitrogen ambient. The nitrogen concentration in the nitrogen-doped wafers was measured by secondary ion mass spectrometry (SIMS) performed by Evans Analytical Group. The detection limit was 5×10^{13} cm^{-3} and three measurements were made in each location.

One nitrogen-doped FZ wafer was RCA cleaned and annealed at 1000 °C for 1 h under nitrogen ambient. Following the high temperature anneal, the nitrogen-doped FZ wafer was etched in 5 wt% HF to remove any SiO_2 film. All wafers were then RCA cleaned. One (nonannealed) nitrogen-doped FZ wafer was used to study the effect of hydrogenation on the defect density and was coated with plasma-enhanced chemical vapor-deposited (PECVD) silicon nitride (SiN_X:H at 235 °C for 1 h). The other wafers were coated with atomic-layer-deposited (ALD) aluminum oxide (Al_2O_3:H) deposited at 200 °C and subsequently activated at 400 °C in forming gas for 30 min, in order to activate the surface passivation.

Effective lifetime measurements were performed using the transient photoconductance method [23]. The lifetime

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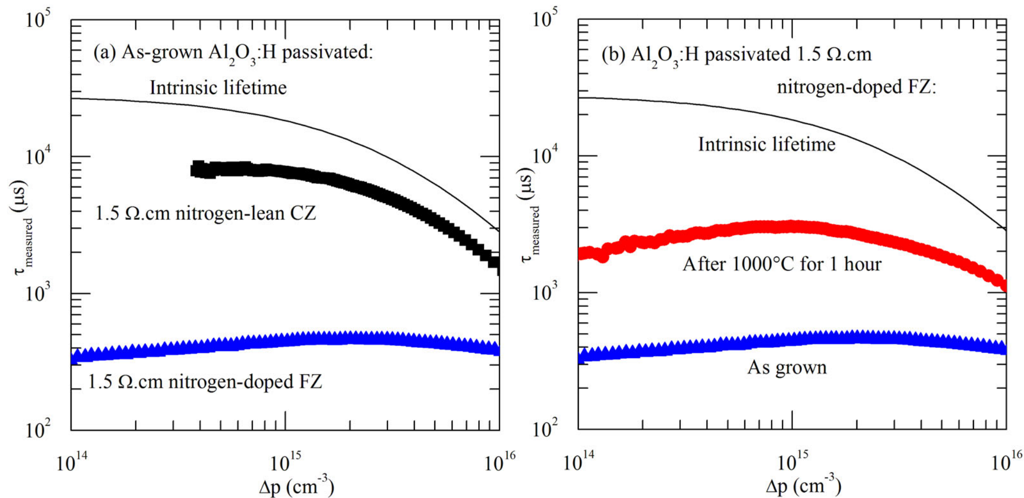

Fig. 1. (a) Injection dependence of the measured lifetime for nitrogen-lean n-type Cz silicon and FZ nitrogen-doped n-type silicon. (b) Injection dependence of the measured lifetime: before and after annealing at 1000 °C for 1 h. The intrinsic lifetime limit [1] is plotted as a solid line on both graphs.

measurements were obtained with a Sinton WCT120 system, where the sensing area has a diameter of 4 cm. PL lifetime images were obtained using a BT Imaging LIS-R1 system [24]. For PL imaging, the lifetime was measured at low injection, where the lifetime is less injection dependent. Considering the excellent passivation quality, the effective defect concentration was calculated as $N_t^* = 1/\tau_{\text{residual}} = 1/\tau_{\text{measured}} - 1/\tau_{\text{intrinsic}}$ using a recent intrinsic (Auger and band-band) lifetime parameterization [1].

III. Results

A. *Influence of Nitrogen on the Minority Carrier Lifetime in as-Grown and Thermally Processed Silicon*

Fig. 1(a) shows the measured injection dependence of the lifetime of the Cz wafer and the nitrogen-doped FZ wafer. The lifetime of the nitrogen-doped sample in the as-grown state is clearly limited by recombination active defects. The oxygen and carbon concentrations are expected to be significantly lower than 1×10^{16} cm^{-3} and are below the detection limit of standard SIMS or Fourier transform infrared spectroscopy measurements. However, nitrogen concentrations of 4.6×10^{14} cm^{-3} were measured with SIMS in this nitrogen-doped wafer. Hence, it is possible that nitrogen plays a role in the observed recombination active defect.

Fig. 1(b) shows the measured-injection dependent lifetime of the samples before and after annealing at 1000 °C for 1 h (passivated with Al_2O_3:H). The lifetime increases from 450 μs to above 3 ms. Provided the recombination active defect observed is nitrogen related, this change in lifetime could correspond to the defect transformation observed by others in nitrogen-doped FZ silicon using deep level transient spectroscopy (DLTS) [17]. Such behavior was observed in as-grown FZ silicon doped with nitrogen, but not in nitrogen-free FZ silicon [17], [18] and was shown to disappear after 900 °C anneal for 3 h [17]. Its concentration was also found to scale with the N concentration and to be in concentrations of $7 \times 10^{11} - 8 \times 10^{11}$ cm^{-3} (for total nitrogen concentrations of 1.9×10^{15} cm^{-3}) [17].

The majority nitrogen species in silicon is the split interstitial dimer [25]. The recombination activity in our samples is not consistent with recombination through a defect with a $\sim 10^{14}$ cm^{-3} concentration, as this would require the defect to have unphysically small capture cross sections. Our study is, thus, further evidence for the nitrogen dimer not having any states in the gap [26]. Therefore, our defect, if nitrogen related, is most likely a minority nitrogen-containing species.

B. *Spatial Distribution of the Defect Density and Potential Composition of the Defect*

In order to better understand the composition of the defect, the spatial distribution of the lifetime and the defect density were then measured. Fig. 2(a) and (b) shows the spatial distribution of the lifetime of the unprocessed nitrogen-doped wafer passivated with aluminum oxide (including 400 °C activation step) and silicon nitride, respectively. In both cases, the lifetime is significantly lower in the center of the wafer compared with the edge. The lifetime in the Al_2O_3:H-passivated sample is also about one order of magnitude lower than in the SiN_X:H-passivated samples, and this will be addressed later. Fig. 2(c) shows the profile of the effective defect density from the center to the edge of the wafer. It also shows the SIMS measurements at the center and the edge of the wafer (three measurements at each location). While the nitrogen concentration remains almost constant laterally, the recombination center concentration is significantly higher in the center of the wafer. Such a reduction of the defect density near the edges of the wafer has been observed before in nitrogen-doped FZ silicon using DLTS, where it was attributed to a reduced vacancy concentration (or increased interstitials) near the edges, reducing the concentration of the vacancy nitrogen complexes [20]. Indeed in vacancy-rich growth mode (which is standard for rapidly-grown floating zone crystals), the vacancy concentration is greater in the center of the wafer [13], [16], [27], [28] and is likely to show a similar distribution as the effective defect concentration in Fig. 2(c). This suggests that nitrogen complexed with

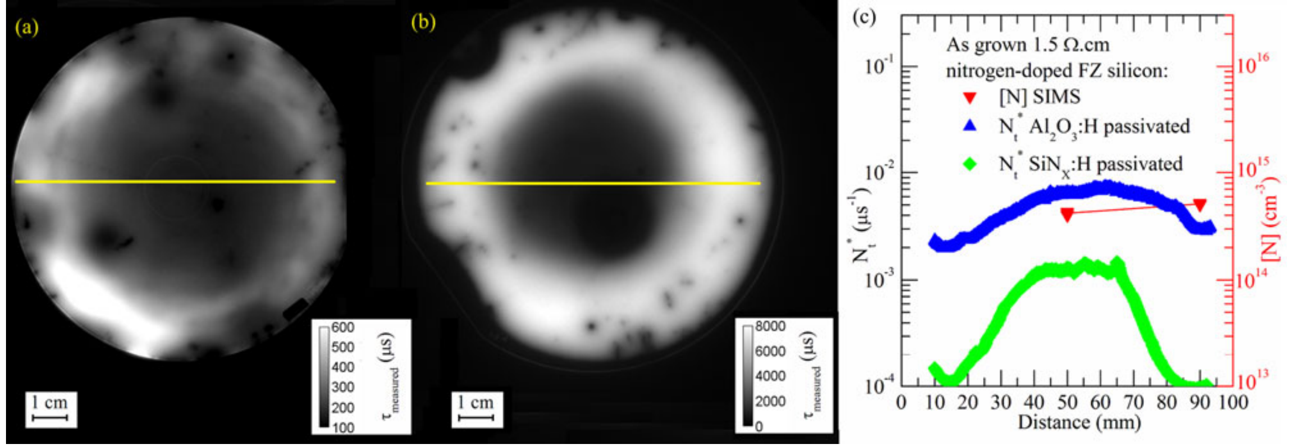

Fig. 2. Low-injection PL image of the nitrogen-doped FZ silicon sample before annealing with (a) Al_2O_3:H passivation and (b) SiN_X:H passivation. Lifetimes are measured in μs. (c) Profile of the effective defect density is plotted across the wafer, and the SIMS nitrogen measurements at the two tested regions are also plotted.

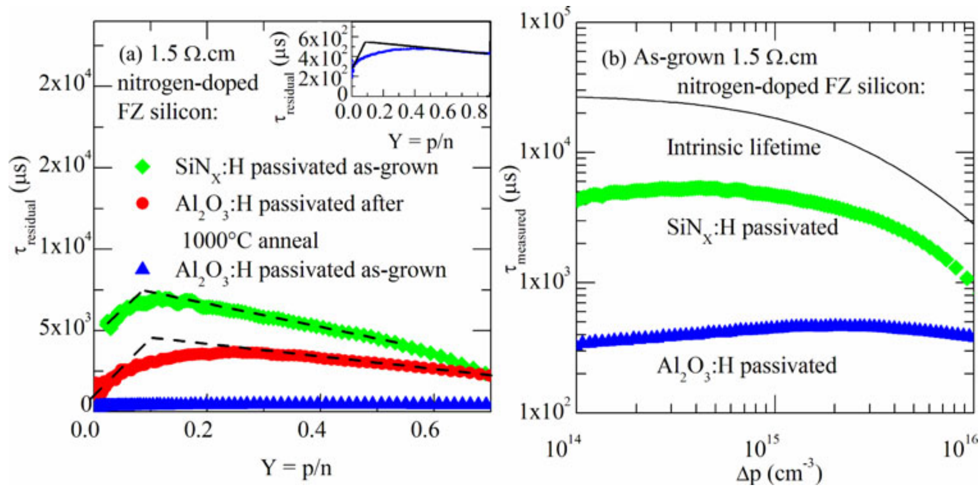

Fig. 3. (a) Residual minority carrier lifetime as a function of the p/n ratio before and after annealing at 1000 °C for 1 h and after the deposition of a hydrogen containing film SiN_X:H. (b) Injection dependence of the measured lifetime before and after the deposition of a hydrogen containing film SiN_X:H. The line on (b) represents the intrinsic limit [1]. The lifetime increases significantly after the hydrogenation procedure.

vacancies could constitute the observed recombination active defect.

C. One or Many Defect Species?

There have been many different complexes between vacancies and nitrogen identified previously ($V_X N_Y$) [26]. The question remains whether only one species is responsible for the observed low lifetime, or if a combination of different defects is responsible. Fig. 3(a) shows the measured injection dependence of the lifetime, corrected for intrinsic recombination, as a function of the ratio of total hole concentration (p) to the total electron concentration (n). A linear behavior in such a plot would imply the existence of just one single-level defect [9]. The absence of a single linear trend over the whole injection range suggests that at least two defects (or perhaps one defect with two levels) are responsible for the observed reduced lifetime [9]. The defect parameters cannot be determined in this case, as this requires the availability of samples with significantly different doping levels.

D. Hydrogenation of the Defect

Regardless of their structure, the observed defect(s) has(have) the potential to significantly degrade the performance of high-efficiency n-type silicon solar cells, especially rear-junction solar cells, which are most sensitive to the carrier lifetime in the wafer bulk. However, such cells are likely to incorporate a deposition step of silicon nitride, amorphous silicon or aluminum oxide, potentially leading to partial hydrogenation of the bulk. Such hydrogenation could potentially alter the recombination activity of the nitrogen-vacancy centers.

In order to test the potential effect of hydrogen on the nitrogen-related defect, we have applied films with different hydrogen content and studied the changes in carrier lifetime. It is known that PECVD-deposited SiN_X:H and ALD-deposited Al_2O_3:H not only have different total (atomic and paired) hydrogen concentrations (15–20% for SiN_X:H versus $<5\%$ for Al_2O_3:H) [29], [30], but the indiffusion of atomic hydrogen in the wafer is also different due to plasma damage [31]. Fig. 3(b)

shows the injection dependence of the lifetime for samples passivated with these two films. Note that photoconductance-based lifetime measurements (averaged over an area of 4 cm) are affected by spatial lifetime nonuniformities; thus, the shape of the injection dependent lifetime curve may be slightly inaccurate. In any case, the samples which have been passivated with PECVD SiN_X:H have significantly higher lifetimes than the samples passivated with ALD Al_2O_3:H. Measurement on control wafers shows similar passivation for SiN_X:H and Al_2O_3:H; hence, the improved lifetime in the nitrogen-doped wafers is not due to differences in surface passivation. Instead, our results suggest hydrogen may be able to passivate a significant fraction of the recombination active defect(s).

IV. Conclusion

In conclusion, we show that one defect or multiple defects limit(s) the lifetime in highly pure nitrogen-doped n-type floating zone silicon wafers. A very low bulk level of nitrogen ($\sim 5 \times 10^{14}$ cm^{-3}) is suggested to give rise to a minority nitrogen-containing species, which reduces the lifetime from 4.8 ms to below 450 μs at an injection of 1×10^{15} cm^{-3}. By measuring the spatial distribution of the defect, our initial study suggests the most likely candidate for the observed recombination active defect is a vacancy and nitrogen-related defect $V_X N_Y$. We demonstrate that the defect can be removed during high temperature processing of standard silicon solar cells, consistent with previous studies on nitrogen-related defects using DLTS. For low-temperature-processed silicon solar cells, such as heterojunction solar cells, the defect will still be present in the finished solar cell. In order to mitigate the impact of the defect, one can either perform a high temperature annealing prior to processing or a hydrogenation procedure.

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