Injection-dependent carrier lifetime analysis of recombination due to boron-oxygen complexes in wafers passivated with different dielectrics by QSSPL and QSSPC

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Abstract

This paper compares the use of quasi-steady state photoluminescence (QSSPL) and photoconductance (QSSPC) measurements for injection-dependent carrier lifetime analysis of the state of boron-oxygen (B-O) complexes in boron-doped Czochralski wafers passivated with different dielectrics. Use of QSSPL measurements enabled effective carrier lifetime measurements over a larger range of injection levels than possible with QSSPC, potentially increasing the accuracy of estimates of the capture cross-section ratio of the deep-level B-O Shockley-Read Hall (SRH) defect. Although the capture cross-section ratios estimated using QSSPL (9.7 ± 1.7) and QSSPC (9.7 ± 1.9) for wafers symmetrically-passivated with silicon nitride and subsequently rapidly fired were very similar and close to the value of 9.3 reported by Rein et al. for the B-O defect, significant differences in the ratio and larger variances in the measurements within a group resulted for wafers with silicon nitride that was not annealed and wafers which were passivated with the thermal oxide. It is suggested the low-injection QSSPL measurements may introduce inaccuracies arising from the conduction of excited carriers via the diffused emitter away from the measurement area. This may suggest that there is little advantage in using QSSPL over the more commonly-used QSSPC measurements for these SRH analyses. Additionally, the study confirmed that stable regeneration of the effective carrier lifetime was only achieved when wafers were passivated with silicon nitride and underwent a rapid thermal anneal after deposition. If wafers were not rapidly thermally-annealed after silicon nitride deposition, then the recovery of effective lifetime observed with regeneration was not stable during a second light soak. Furthermore, the effective carrier lifetime of wafers passivated with a thermal oxide continued to decrease with light soaking, regeneration and a second light soaking with the appearance of “rings” in the PL images of oxide-passivated wafers as they underwent light soaking and regeneration highlighting the possible role of oxide precipitates in reactions occurring with light soaking and regeneration.

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1. Introduction

It was shown in [3] that analysis of injection-dependent effective minority carrier lifetimes, $\tau_{\text{eff}}$, measured by a combination of quasi steady state (QSS) photoluminescence (PL) and QSS photoconductance (PC), can be used to identify different recombination states of boron-oxygen (B-O) complexes providing recombination at the wafer surfaces is minimised. The introduced recombination due to light soaking was modelled as a single Shockley-Read-Hall (SRH) recombination centre corresponding to the deep-level B-O complex at $E_c - E_t = 0.41 \text{ eV}$ [4, 5], the analysis resulting in an estimate for the electron:hole capture cross section ratio ($\sigma_n: \sigma_p$) of $\sim 14$ for the introduced defect (compared to a value of 9.3 reported in [5]). However, in the study reported in [3], wafers were not symmetrically-passivated so it was difficult to definitively separate surface effects from bulk effects.

In this study, injection-dependent measurements of $\tau_{\text{eff}}$ were obtained using both QSSPL and QSSPC and used to estimate the $\sigma_n: \sigma_p$ of the B-O complex following the steps of light soaking and regeneration [6, 7] in symmetrically phosphorus-diffused wafers with SiN$_x$ layers deposited by plasma-enhanced chemical vapour deposition (PECVD) and thermally-grown SiO$_2$ layers. Nampalli et al. [8] showed that a hydrogen source and illuminated thermal annealing are required for stable regeneration of the deep-level B-O defect. Consequently, it was hypothesised that a SRH recombination analysis of injection-dependent $\tau_{\text{eff}}$ may be able to provide further evidence for the requirements of a hydrogen-containing dielectric to achieve stable regeneration. In initial experiments, in which wafers passivated with thermal oxide underwent a rapid thermal anneal, the oxide surface passivation was degraded making it difficult to discern changes occurring in the bulk due to light soaking and regeneration. Consequently in this study, a rapid thermal anneal (RTA) was not performed after the thermal oxidation step. This resulted in low surface recombination velocities thereby enabling changes in bulk recombination to be observed in the injection-dependent $\tau_{\text{eff}}$. As reported in [3], the SRH defect was modelled using both the pre-light soaked state and the regenerated state as the initial state, the latter analysis providing insights as to whether the regeneration process changed the recombination properties of defects other than the B-O defect.

An objective of the study was to compare the accuracy of the $\sigma_n: \sigma_p$ values estimated using QSSPL and QSSPC, the QSSPL measurements being performed over the larger injection level range of $\sim 2 \times 10^{11}$ to $\sim 10^{17} \text{ cm}^{-3}$. We assess errors introduced by using QSSPL measurements at low injection levels where parasitic effects such as non-uniform illumination of the full wafer can reduce the accuracy of the low injection PL measurements due to highly conductive paths existing between the illuminated area and dark regions of the wafer [9]. The use of lower injection data may also reduce the validity of the assumption that a single recombination centre is introduced by the light soak and regeneration process as it increases the probability that the measured $\tau_{\text{eff}}$ data is influenced by changes arising from more than one recombination centre.

2. Experimental

2.1. Substrate preparation

Alkaline-textured 156 mm 1-3 $\Omega$ cm boron-doped Czochralski (Cz) wafers were phosphorus-diffused to form symmetrical emitters having a sheet resistance of $\sim 120 \Omega/\square$. A RTA at 700 °C was performed after diffusion [with the phosphosilicate glass (PSG) in place] in a belt furnace to ensure that all the wafers were in an identical annealed state before the high temperature oxidation as the thermal history of the wafers was not known. After PSG removal, a 200 nm thermal oxide was grown on all wafers at a temperature of 950 °C for 30 min and then wafers were divided into three groups. The oxide was removed from the surfaces of the Group A and B wafers and a 75 nm thick SiN$_x$ layer having a refractive index of 2.09 was deposited on both wafer surfaces in a remote PECVD chamber (Roth & Rau MAiA) at 400 °C. The Group A wafers then received a further RTA at 700 °C for a period of 2-3 s. All wafers were light-soaked for 2 days at 0.7 to 0.9 suns and then the regeneration process [7] was performed at 0.7 suns (using a halogen lamp) at 200 °C for 30 min. Finally, the light soaking step was repeated to establish the stability of the regeneration process. This processing flow is summarised in Fig. 1.

After each processing step QSSPL and QSSPC measurements were performed as described in [3]. For each wafer, the recombination current density at the surface, $J_{0s}$, was extracted from the high injection data [10] to assess the effect of the different processing steps on the surfaces. Then the injection dependent $\tau_{\text{eff}} (\Delta\nu)$ of the light-soaked
state was modelled assuming the introduction of a single SRH defect having a trap energy \( E_t \) corresponding to the deep-level B-O defect using:

\[
\frac{1}{\tau_{\text{eff}}(\Delta n)} = \frac{1}{\tau_{\text{eff},0}(\Delta n)} + \frac{N_A + \Delta n}{\tau_{p0}(n_1 + \Delta n) + \tau_{n0}(N_A + p_1 + \Delta n)}
\]

where \( \tau_{p0} \) and \( \tau_{n0} \) represent the lifetimes of electron and holes at the defect, and \( n_1 \) and \( p_1 \) are the equilibrium electron and hole density, respectively, when the Fermi level coincides with the energy of the recombination centre.

Figure 2 illustrates how the light-soaked state was modelled using either the pre-light-soaked state or the regenerated state as the initial state. To determine whether use of QSSPL data increases the accuracy of the SRH analysis, the data fits were performed using each of the QSSPL data (recorded from \( \sim 2 \times 10^{11} \) to \( \sim 10^{17} \text{ cm}^{-3} \)) and QSSPC data (recorded from \( 2-3 \times 10^{14} \text{ cm}^{-3} \) to \( \sim 10^{17} \text{ cm}^{-3} \)).

Fig. 1. Flow chart showing the processing steps for the different groups.

Fig. 2. Schematic showing how the light-soaked injection-dependent \( \tau_{\text{eff}} \) was modelled using from a pre-light soaked state (Method I) and from the regenerated state (Method II). In all cases \( E_t \) was assumed to be 0.41 eV below \( E_c \).
3. Results and discussion

3.1. Complications arising from processing

The experiment commenced with 18 wafers randomly picked from a set of 100 p-type Cz wafers. After the thermal oxidation step, rings were observed to different extents in the photoluminescence (PL) images for a number of the wafers (see Fig. 3). Such rings can form due to recombination at iron-decorated oxygen precipitates and surrounding crystal defects [2, 11-13]. Most industrial Cz wafers contain iron which is typically fortuitously gettered to the emitter by the phosphorus diffusion step. However, in the processing sequence used here, gettered iron may have been released back into the bulk of the wafer during the thermal oxidation, from where it is either gettered to or precipitated at oxygen precipitates which form in rings corresponding to vacancy-rich regions which can occur in rapidly-grown ingots. Recombination in iron-contaminated samples has been shown to depend both on the concentration of iron and the density of oxide precipitates [14]. Murphy et al. proposed that if the iron concentration is relatively low (< 5 x10^{12} cm^{-3}) then iron can be gettered (reversibly) at the precipitates but higher contamination levels can result in irreversible precipitation [13]. In this study, the pre-oxidation RTA may have exacerbated this situation by initiating the nucleation of more oxygen precipitates than would have otherwise have been present.

The extent of this problem varied between wafers, most likely as a result of differences in both the oxygen and iron concentrations between wafers. However, it was interesting to note that when SiNx was deposited on 12 of the initial 18 wafers, the wafers having the most evident rings after thermal oxidation experienced a very large decrease in \( \tau_{\text{eff}} \) with the entire centre of the wafer being seriously degraded in PL intensity [see Fig. 3(c)]. Annealing after SiNx deposition (for Group A wafers) improved these wafers’ \( \tau_{\text{eff}} \) slightly, but the improvement was mostly in the peripheral regions than in the central regions of the wafer. This observation supports the theory that although hydrogen may be able to passivate dangling bonds associated with oxide precipitates [13, 15], it may be less effective at reducing recombination at iron-decorated oxide precipitates. To minimise the effect of this problem on the remaining experiment, all the wafers in which rings were evident in the PL images either immediately after thermal oxidation or after SiNx deposition were eliminated from the subsequent analysis. This left only three wafer per group.

![Fig. 3. Images (a) and (b) show two wafers after the thermal oxidation step. The wafer in (a) shows evidence of annular regions of reduced \( \tau_{\text{eff}} \), whereas the wafer in (b) is reasonably uniform except for edge effects. The PL images in (c) and (d) were recorded after 75 nm SiNx had been deposited (i.e., after SiO\(_2\) removal). Whereas the \( \tau_{\text{eff}} \) of the wafer imaged in (c) is seriously degraded especially in the centre of the wafer, there is no evidence of “rings” in (d). All PL images were recorded using a BTi imaging tool with a 0.1s exposure and are graphed using the same scale.](image-url)
3.2. Injection-dependent effective lifetime measurements

Figure 4(a) shows the injection-dependent \( \tau_{\text{eff}} \) for representative wafers from each group of wafers and Table 1 lists the implied open circuit voltage, \( iV_{\text{OC}} \), and \( J_0 \) for each group after each process. Low \( J_0 \) values of 4 fA/cm\(^2\) were measured for both the SiN\(_x\)-coated and the thermal oxide-coated wafers, though for SiN\(_x\), it was necessary for the wafers to be annealed after deposition to achieve these low surface recombination currents. The first light soak did not change \( J_0 \) for Group A and C wafers, suggesting that the decrease in \( iV_{\text{OC}} \) that was measured was due to the introduction of recombination within the wafer, presumably largely due to the activation of B-O defects. However, for the Group B wafers, \( J_0 \) increased with light soaking therefore making it difficult to determine where the introduced recombination was occurring.

The regeneration process increased the \( \tau_{\text{eff}} \) and \( iV_{\text{OC}} \) of the SiN\(_x\)-coated wafers (see Fig 4 (a) and (b)) but further degraded the \( iV_{\text{OC}} \) of the thermal-oxide passivated wafers [see Fig. 4 (c)]. Furthermore, the regenerated \( iV_{\text{OC}} \) was only stable during a 2\(^{nd}\) light soaking for Group A wafers (SiN\(_x\) with a subsequent RTA), with the thermal oxide passivated wafers degrading even further with the 2\(^{nd}\) light soaking. This result adds further evidence to the theory that a “fired” hydrogen dielectric is required for stable B-O regeneration. Some recovery in \( iV_{\text{OC}} \) after regeneration was possible if the deposited SiN\(_x\) was not rapidly annealed (Group B) before light soaking but this recovery was not stable. It was also observed that during the process of light soaking/regeneration/light soaking, ‘rings’ started to appear in the SiO\(_2\) passivated wafers (Group C) becoming progressively more evident with each step (see Fig. 6). This raises the possibility that carrier injection with thermal annealing may also be enhancing impurity decoration of oxide precipitates, a possibility which requires further investigation. “Rings” did not become more evident in the PL images after light soaking and regeneration in the Group A and B wafers.

![Fig. 4 Injection-dependent \( \tau_{\text{eff}} \) measured using QSSPL and PC for a representative wafer from: (a) Group A (SiN\(_x\) with subsequent RTA); (b) Group B (SiN\(_x\) and no subsequent RTA); and (c) from Group C (thermal oxide).](image)

<table>
<thead>
<tr>
<th>Process</th>
<th>Group A</th>
<th>Group B</th>
<th>Group C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( iv_{\text{oc}} ) (mV)</td>
<td>( J_0 ) (mA/cm(^2))</td>
<td>( iv_{\text{oc}} ) (mV)</td>
</tr>
<tr>
<td>After thermal oxidation</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>After SiN(_x) deposition</td>
<td>657 ± 2</td>
<td>59 ± 6</td>
<td>654 ± 2</td>
</tr>
<tr>
<td>After RTA</td>
<td>678 ± 2</td>
<td>4 ± 1</td>
<td>NA</td>
</tr>
<tr>
<td>1st Light soak</td>
<td>671 ± 1</td>
<td>4 ± 1</td>
<td>643 ± 1</td>
</tr>
<tr>
<td>Regeneration</td>
<td>676 ± 1</td>
<td>4 ± 1</td>
<td>650 ± 1</td>
</tr>
<tr>
<td>2nd Light soak</td>
<td>675 ± 1</td>
<td>4 ± 1</td>
<td>644 ± 2</td>
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3.3. SRH modelling of changes with light-soaking and regeneration

SRH modelling was performed for both the QSSPL and the QSSPC data. For all wafers, the light-soaked $\tau_{\text{ef}} (\Delta n)$ data were modelled assuming the introduction of a single SRH defect ($E_c - E_t = 0.41$ eV) and initial states of: (i) the pre-light-soaked state; and (ii) the regenerated state. This resulted in estimates of $\sigma_n, \sigma_p$ for each wafer which were averaged for each group (see Table 2). Although the increased range of data obtained from the QSSPL might be expected to result in a more accurate estimate of $\sigma_n, \sigma_p$, the low injection data may be impacted by recombination at the wafer edges or regions outside of the illuminated area [9]. This recombination can be more significant for diffused wafers (as used here) as carriers are more effectively conducted out of the PL detection region. To minimise the impact of such recombination, the measurements were performed on 156 x156 mm wafers. The average $\sigma_n: \sigma_p$ ratio estimated for the Group A wafers was $9.7 \pm 1.7$ and $9.7 \pm 1.9$ using the QSSPL and QSSPC data, respectively. These estimates for $\sigma_n, \sigma_p$ were very close to the previously-reported value of 9.3 reported by Rein et al. [5]. Comparison of the resulting values and uncertainty’s between the QSSPL and QSSPC data demonstrates that an improved value was not achieved from the significantly larger injection range of the QSSPL data. Figure 6(a) shows the data fit (black line) with the QSSPL data for initial (after RTA; green symbols) and light-soaked state (blue symbols). The estimated $\sigma_n, \sigma_p$ for this wafer was $10.1 \pm 0.9$, the error being calculated from the covariance matrix of the least squares fit [16].

Figure 7 shows the analyses that were performed for the same wafers as used for Fig. 6 using the regenerated state as the initial state. There was a much larger difference in the $\sigma_n: \sigma_p$ value estimated using QSSPL ($10.0 \pm 0.7$) and QSSPC ($15 \pm 0.4$) in this case. This difference may be due to the regeneration process also affecting recombination at other defects, and in particular defects which influence the lower injection regions of the curves. This may have limited the accuracy and validity of the QSSPL modelling as the initial assumption of a single introduced defect was no longer valid. The average values of $\sigma_n: \sigma_p$ estimated using the QSSPL and QSSPC measurements were both higher than that estimated using the RTA state suggesting that the regeneration process is not simply eliminating the recombination introduced by light soaking. The increased variance in the individual estimates may arise due to different impurities/defects being in the individual wafers.

Figure 8 compares the estimates of $\sigma_n: \sigma_p$ obtained using the QSSPL and QSSPC measurements for all groups of wafers with Fig. 8(a) using the pre-light-soaked state as the initial state and Fig. 8(b) using the regenerated state as the initial state. The larger variance when using the QSSPL data may be due to inaccuracies introduced by the
measurement of low-injection QSSPL data. If the objective of the analysis is to accurately estimate the $\sigma_n:\sigma_p$ for the deep-level B-O defect then a practical solution is to only measure the range where the expected asymmetric $\sigma_n:\sigma_p$ is expected to be manifest in the $\tau_{\text{eff}}(\Delta n)$ data. If that can be achieved using QSSPC then use of QSSPL may introduce unnecessary complications and reduce accuracy.

The larger values of $\sigma_n:\sigma$ estimated for Group A when the regenerated state was used as the initial state suggests that the regeneration process is affecting more than the deep-level B-O defect. The larger variance in these estimates is consistent with recombination changes with regeneration that may depend on the presence of impurities and/or oxide precipitates in the wafers.

Fig. 6. Injection-dependent $\tau_{\text{eff}}$ measured by QSSPL (a) and QSSPC (b) representing the best fit of Eq. 1 to the first light-soaked data using the RTA state as the initial state [i.e., Method I in Fig. 2]. The value of the $\sigma_n:\sigma_p$ was estimated to be $10.1 \pm 0.9$ and $8.5 \pm 0.5$ for (a) and (b) respectively.

Fig. 7. Injection-dependent $\tau_{\text{eff}}$ measured by QSSPL (a) and QSSPC (b) representing the best fit of Eq. 1 to the first light-soaked data from using the regenerated state as the initial state [i.e., Method II in Fig. 2]. The value of the $\sigma_n:\sigma_p$ was estimated to be $10.0 \pm 0.7$ and $15 \pm 0.4$ respectively.
Table 2: Estimated $\sigma_n/\sigma_p$ ratios by QSSPL and QSSPC assuming the introduction of a single defect corresponding to the B-O defect ($E_c - E_t = 0.41$ eV) being introduced into the pre-light-soaked state and regenerated state. The errors in the estimates for $\sigma_n/\sigma_p$ represent the maximum deviation from the computed mean of the wafers in each group.

<table>
<thead>
<tr>
<th>Group</th>
<th>From pre-light-soaked state</th>
<th>From regenerated state</th>
<th>From pre-light-soaked state</th>
<th>From regenerated state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group A</td>
<td>$9.7 \pm 1.7$</td>
<td>$20.0 \pm 11.3$</td>
<td>$9.7 \pm 1.9$</td>
<td>$18.5 \pm 4.5$</td>
</tr>
<tr>
<td>Group B</td>
<td>$16.6 \pm 1.7$</td>
<td>$12.9 \pm 10.8$</td>
<td>$13.8 \pm 2.8$</td>
<td>$13.7 \pm 1.3$</td>
</tr>
<tr>
<td>Group C</td>
<td>$23.3 \pm 3.5$</td>
<td>NA</td>
<td>$15.7 \pm 10.3$</td>
<td>NA</td>
</tr>
</tbody>
</table>

4. Conclusion

The use of QSSPL to increase the range over which $\tau_{\text{eff}} (\Delta n)$ was measured did not necessarily result in an improved accuracy of estimates of $\sigma_n/\sigma_p$. Rather the inclusion of lower-injection data, where the effects of recombination outside of the PL detection region become significant [9], prevent accurate measurement of the change in $\tau_{\text{eff}}$ and therefore accurate estimation of $\sigma_n/\sigma_p$.

This study provides further evidence for the need to provide a source of hydrogen and to perform a RTA after the application of the hydrogen-rich dielectric to achieve stable regeneration of the B-O defect. If wafers were passivated with a SiNx layer which was not fired, then the recovery of $iV_{\text{oc}}$, observed with regeneration, was not stable during a second light soak and the $iV_{\text{oc}}$ of wafers passivated with a thermal oxide continued to decrease with light soaking, regeneration and a second light soaking. A SRH analysis of the injection-dependent $\tau_{\text{eff}}$, which assumed that light soaking introduced a single defect (from the pre-light-soaked state) with an $E_t$ corresponding the deep-level B-O defect, resulted in a $\sigma_n/\sigma_p$ estimate of $9.7 \pm 1.7$ and $9.7 \pm 1.9$ obtained from both QSSPL and QSSPC for wafers symmetrically-passivated with SiNx and subjected to a RTA after deposition. These values are very similar to the value of $9.3$ reported by Rein et al. [5]. The larger value of $\sigma_n/\sigma_p$ for SiNx-coated wafers (Group A) and the greater variance when the regenerated data was used as the initial state suggested that the regeneration process is affecting more than the deep level B-O defect.

Finally, the inclusion of the thermal oxidation step in this study has highlighted the possible role of oxide precipitates in reactions occurring with light soaking and regeneration. The appearance of “oxide rings” in the PL images of wafers passivated with a thermal oxide as they underwent light soaking and regeneration suggests that carrier injection may cause impurity decoration of oxide precipitates, a possibility that requires further investigation. The thermal oxidation step after phosphorus diffusion introduces further complications in that it can release gettered
metal back into the base of the wafer where it can influence and contribute to recombination changes during processing. Accurate estimates of $\sigma_n$, $\sigma_p$ using QSSPC or QSSPL requires that gettering and oxide precipitation must be carefully controlled. This can be challenging to achieve in practice.

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References