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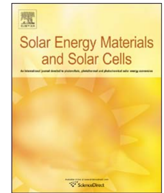

Recent insights into boron-oxygen related degradation: Evidence of a single defect

Brett Hallam[a,*], Moonyong Kim[a], Malcolm Abbott[a], Nitin Nampalli[a], Tine Nærland[b,1], Bruno Stefani[a,c], Stuart Wenham[a]

[a] School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, Sydney, NSW 2052, Australia
[b] Institute for Energy Technology, Instituttveien 18, 2007 Kjeller, Norway
[c] School of Engineering, Federal University of Rio Grande do Sul, Porto Alegre, Brazil

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ABSTRACT

Fast and slow boron-oxygen related degradation in p-type Czochralski silicon is often attributed to two separate defects due to the different time constants and the determination of different capture cross section ratios (k). However, recent work has suggested the possible involvement of a single defect [1,2]. This study reviews recent evidence, and provides further evidence/analysis to demonstrate the involvement of a single defect, in four key areas: 1) Identical recombination properties in the fast and slow timescales [1]; 2) The ability to describe a multi-stage degradation of carrier lifetime with a single recombination active defect [1]; 3) The possible involvement of interstitial iron in accounting for higher apparent capture cross-section ratios during early stages of boron-oxygen related degradation and recombination with a high capture cross-section ratio remaining after permanent deactivation; 4) The ability to modulate the fraction of fast and slow degradation by thermal annealing without modulating the total extent of degradation or recombination properties [2]. A revised parameterisation of the B-O related recombination is also presented, which suggests a stronger influence of acceptor-level related recombination than has been previously reported.

1. Introduction

Boron-oxygen (B-O) related degradation has been studied for decades, with early identification of the degradation mechanism dating back to 1973 [3]. However, there is still significant debate over the structure, formation and passivation mechanisms for the defect [4–7]. One well-understood property of the degradation is that the presence of both oxygen and boron in Czochralski (Cz) silicon can cause a reduction of minority carrier lifetime in the presence of carrier injection [3,8]. Full degradation of the minority carrier lifetime can take approximately 48 h at room temperature. On finished PERC solar cells, this can cause a reduction in efficiency of 1.8% absolute, representing a performance degradation that can approach 10% relative [3,9].

A well-known characteristic of B-O related degradation is that it occurs in two stages [10]. This degradation consists of a fast but slight decay of minority carrier lifetime with a time constant in the vicinity of 100 s, followed by a substantially slower and much more significant reduction of carrier lifetime with a time constant on the order of tens of hours [10–14]. For studies investigating the extent of fast and slow degradation, a linear dependence on the boron doping concentration was observed [11,15].

Another well-known characteristic related to B-O defects is that on a pre-degraded sample, thermal annealing in the dark on can lead to a recovery of minority carrier lifetime, in a process called defect ‘annihilation’ [3,9,16–18]. However, this recovery is unstable, and exposure to subsequent carrier injection again results in a degradation of the minority carrier lifetime. The annihilation rate of B-O defects has been intensively investigated, although there is a significant spread in the values reported for the associated attempt frequency and activation energy [8,10,11,19–23]. A condition known to result in the full recovery of minority carrier lifetime after B-O related degradation is an anneal at 200 °C for 10 min in the dark [24]. A large number of studies investigating B-O related degradation have used this condition [7,11,18,20,25–27]. Numerous other studies have used the same temperature for longer durations in the range of 20 min to 100 h [13,15,28–34]. Other studies have used different temperatures in the range of 210–300 °C [35–38] and also 100–400 °C [39]. For the kinetics of the recovery process, one study observed a two-staged recovery of carrier lifetime for the fast decay and a single-staged recover for the slow decay [11], while another study reported that the lifetime

* Corresponding author at: Ira A. Fulton, Schools of Engineering, Arizona State University, Tempe, AZ 85287, USA.
1 Present address: Ira A. Fulton, Schools of Engineering, Arizona State University, Tempe, AZ 85287, USA

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Nomenclature

B-O	Boron-oxygen
DA	Dark Annealed
DG	Full Degradation
FRC	Fast-forming Recombination Centre
LS(t)	t seconds of Light Soaking
ODE	Ordinary Differential Equations
S1DP	Stage 1 Defect Precursor
S2DP	Stage 2 Defect Precursor
SRC	Slow Forming Recombination Centre
A1	State consisting of Stage 1 Defect Precursors
A2	State consisting of Stage 2 Defect Precursors
B	State of Formed Defect Complex
a	Acceptor Trap
E_t	Energy Level of the Trap
d	Donor Trap
f^0	Fractional Concentration of B-O Defects in the Neutral Charge
FDD	Fractional Defect Density
G	Generation Rate of Electron-Hole Pairs
J_0	Saturation Current Density
k	Capture Cross Section Ratio
κ	Reaction rate
Δn	Excess Charge Carrier Density
N	Normalised Concentration
NDD	Normalised Defect Density
σ_n	Electron Capture Cross Section
σ_p	Hole Capture Cross Section
τ	Charge Carrier Lifetime
τ_{ratio}	Ratio of lifetime in high and low injection
ν	Characteristic Time Constant
W	Thickness of Wafer

recovery occurred in one stage for both the fast and slow decay [10]. However, none of the above studies investigated the influence of modulating the dark annealing temperature on the fast and slow degradation behaviour.

In 2006, a study by Bothe *et al.* examined the recombination properties throughout B-O related degradation [11]. It was concluded that the fast and slow B-O related degradation was caused by two separate defects that form independently [11]. Often, these are called the fast-forming recombination centre (FRC) and the slow-forming recombination centre (SRC) [14,40]. In addition to the differing time constants, one key argument presented for the existence of two separate defects was the determination of a different value for the ratio of the electron- (σ_n) and hole capture cross-section (σ_p) for the fast and slow B-O related degradation [11]. In early studies, the B-O defect was assumed to have a single defect level. Under this assumption, capture cross-section ratios (k) of approximately 100 and ten were determined for the fast- and slow decays, respectively [11]. However, there are significant variations in the k values reported in the literature for both the fast and slow degradation. For the slow degradation, early studies estimated k values of 5–10 [27,37,41]. More recent studies have estimated higher k values in the range of 10–12 [42], or 14 [43]. For the rapid degradation, a subsequent study presented values in the range of 65–86 [44], while a more recent paper by the same author estimated a value of 65 [43].

The variations of k values presented in the literature can at least be partially accounted for by the various assumptions and methods used in the respective papers. A numerical analysis of B-O defect recombination properties presented by Nampalli *et al.* highlighted that illuminated processes could also lead to small, yet statistically significant changes in the surface passivation throughout degradation that breaks the assumption of many methods used to analyse the B-O defect [45]. That paper highlighted that depending on the method used, median values in the range of 12–15 could be obtained.

Another source of error for the determined k values is the assumption of a single level defect for the B-O defect. An early study by Schmidt *et al.* observed that in some samples a shallow level defect was present in addition to a deep level defect [37]. That defect level was observed to decrease the lifetime at high carrier concentrations while having minimal effect at low carrier concentrations. More recent investigations have identified the existence of three defect charge states, and hence two separate defect levels for B-O related degradation in both the fast and slow timescales [44,46]. While the donor level dominates recombination in low-injection, the presence of an acceptor level with a k value < 1 [46] causes a reduction of carrier lifetime predominately at higher injection levels. Therefore, taking the presence of an acceptor level into account will result in the determination of a larger k value for the donor level than that determined when assuming a single defect level.

With different k values and time constants for degradation, multiple subsequent theories have assumed that two separate defects are responsible for the fast and slow decay in carrier lifetime [40,43,44,47,48]. In a recent contribution, another argument was presented. It was suggested that processes to permanently deactivate the B-O complex only remove the combination activity of defects that form in the slow timescale, with recombination activity associated with degradation in the fast timescale, remaining [4].

However, there are also several arguments to suggest a single defect is responsible for both the fast and slow B-O related degradation. This paper aims to review the recent advancements in the understanding of B-O related degradation in silicon solar cells. It collates recent evidence to suggest the existence of a single B-O defect, along with providing more sophisticated modelling and new experimental evidence for the existence of a single B-O related defect. The four key areas in support of this hypothesis are: 1) Identical recombination properties in the fast and slow timescales throughout degradation [1]. 2) Kinetic modelling demonstrating the ability to describe a multi-stage degradation of carrier lifetime [1]. 3) The possible involvement of interstitial iron in accounting for higher apparent k values during early stages of B-O related degradation and recombination with a high k value remaining after permanent deactivation. 4) The ability to modulate the fraction of fast and slow degradation without modulating the total extent of degradation or recombination properties [2].

2. Identical recombination properties of fast and slow B-O related degradation

While earlier studies have presented significant differences in the capture cross-section ratios for degradation in the fast and slow timescales, one striking similarity for recombination properties is the position of the donor and acceptor levels published in some papers (see Table 1). This data provides some evidence for the possibility of a single defect being responsible for B-O related degradation.

Table 1
Defect energy levels for the donor and acceptor levels of the B-O defect reported in the literature for fast and slow degradation.

	$E_{trap,d}$ (eV)	$E_{trap,a}$ (eV)	Ref.
Fast	E_C - (0.38 ± 0.02)	E_V + (0.28 ± 0.02)	[44]
	E_C - (0.34 ± 0.02)	E_V + (0.31 ± 0.02)	[49]
Slow	E_C - (0.41 ± 0.03)		[41]
	E_C - (0.41 ± 0.02)	E_V + (0.26 ± 0.02)	[46]

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