Materials, devices and economics issues for tomorrow's photovoltaics

Lifetime degradation mechanism in boron-doped Czochralski silicon

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Abstract

The recombination centre that emerges in boron- and oxygen-containing silicon was thought to be a complex of a substitutional boron atom $B_s$ and an oxygen dimer $O_2$. However in material co-doped with boron and phosphorus, the degradation parameters were reported to correlate with the hole concentration $p$ rather than with the boron concentration. In the present work, the temperature dependence of the Hall Effect was measured in co-doped and reference samples and the concentrations of isolated acceptors $N_a$ and of donors $N_d$ were deduced. The value of $N_a$ was found to be substantially larger than $p$ and close to the expected total concentrations of boron. This result clearly shows that the reported correlation of the degradation with $p$ implies a lack of correlation with $N_a$. Such a behaviour is accounted for by a model based on formation of $B_iO_2$ complexes (involving an interstitial boron atom $B_i$ rather than $B_s$): the grown-in concentration of this species is proportional to $p$ and independent of $N_a$.

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1. Introduction

Electron lifetime ($\tau$) in boron-doped Czochralski silicon (and more generally, in boron- and oxygen-containing silicon) is known [1,2] to decrease with time in the presence of excess electrons. This is a reason for degradation of efficiency of silicon-based solar cells. The increment of a reciprocal electron lifetime, $R(t) = \frac{1}{\tau(t)} - \frac{1}{\tau(0)}$, tends to a saturated value $R_s$ that was found to depend as $N_B C^2$ on the boron concentration $N_B$ and the oxygen concentration $C$, in boron-only doped samples. A natural attribution of the recombination centre [2] was to a complex $B_2O_2$ of a substitutional boron atom $B_s$ and an oxygen dimer $O_2$. 

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However in p-type material co-doped with boron and phosphorus – to a significant compensation degree – the degradation amplitude $R_e$ was reported [3] to correlate with the hole concentration $p$ rather than with $N_B$. This surprising result was first attributed [3] to a pronounced pairing of boron and phosphorus – such as the concentration $N_B$ of isolated phosphorus donors is much smaller than the total phosphorus concentration $N_P$, and accordingly the concentration $N_B$ of isolated boron acceptors remains close to $p$, in spite of co-doping. In this case the proportionality of $R_e$ to the concentration $N_B$ of isolated boron acceptors would be preserved.

The notion of a strong B-P pairing is however inconsistent [4] with the available data, and it was thus concluded that the concentration $N_B$ of isolated boron acceptors is actually close to the total boron concentration $N_B$ (and the concentration $N_P$ of isolated phosphorus donors is close to the total phosphorus concentration $N_P$). In that case the hole concentration, $p = N_p - N_B$, is essentially smaller than $N_B$ in compensated samples. Hence, a proportionality of the degradation amplitude $R_e$ to $p$ implies that $R_e$ does not correlate with $N_B$. Such a behaviour is not consistent with a BiO$_2$ model of the degrading centre, but it can be accounted for within an advanced model [4] based on formation of single-positive BiO$_2$ complex (involving an interstitial boron atom $B_i$ rather than $B_s$) in the course of crystal cooling. The $B_i$ atoms are produced from $B_s$ by self-interstitials emitted by growing oxide precipitates or clusters, and it is assumed that mobile $B_i$ precipitate themselves, into tiny “nano-precipitates”, leaving only a low dissolved concentration, in equilibrium with these nano-precipitates. This concentration (the solubility) is proportional to $p$ since $B_i$ is a single-positive defect in p-Si [5]. Hence the concentration of grown-in BiO$_2$ defects will follow a $p^{C2}$ dependence, and not an $N_B^{C2}$ dependence. The grown-in BiO$_2$ species are considered as “latent centres” (abbreviated to LC) of a low recombination activity. The degradation is caused by recharging the LC species into neutral state by capturing excess electrons - with subsequent reconstruction into another atomic configuration of BiO$_2$ (denoted SRC) that is recombination-active.

The foundation of the new model is an essential difference between $p$ and $N_B$ in compensated material – a conclusion based on strong and yet indirect arguments [4]. It is then important to obtain more direct evidence – by separate determination of $N_B$ and $N_P$ in compensated samples – and it is the purpose of the present work.

2. Experimental

The samples – two compensated ones and two reference non-compensated ones – were the same as those inspected previously for lifetime degradation in ref.[3, 6]; we keep the original labelling: 44c and 45c for the compensated samples, and 72nc and 73nc for the reference non-compensated ones. They go in two groups: (1) 45c and 72nc - of a higher resistivity (a lower hole concentration, about $10^{16}$ cm$^{-3}$), (2) 44c and 73nc – of a lower resistivity (a higher value of $p$, about $4x10^{16}$ cm$^{-3}$). The Hall coefficient $G$ and the specific resistivity $\rho$ were measured in all the four samples down to the liquid nitrogen temperature. The room-temperature hole concentration will be, from now on, denoted $p_0$, to distinguish it from $p(T)$ at lower $T$. Since $p_0$ is relatively high in the present samples, the Fermi level at $T_{room}$ is not very far from the boron acceptor level, $E_a = E_v + 45.7$ meV (where $E_v$ is the top of the valence band). For this reason, an appreciable hole trapping by the boron acceptors starts very soon upon lowering $T$ below $T_{room}$. Therefore, the inspected temperature range, from $T_{room}$ down to about 80 K, is quite sufficient to trace the temperature dependence $p(T)$ - and to deduce separate values for $N_B$ and $N_P$.

3. Results

The measured Hall coefficient $G(T)$ is related to the hole concentration $p(T)$ by $G = r(\rho p)$, where $e$ is the elementary charge, and $r$ is the so-called Hall factor. At $T_{room}$ the value of $r$ in non-compensated samples is determined using the measured $G$ and $\rho$: the resistivity $\rho$ is converted into $p_0$ by the ASTM (American Society for Testing and Materials) calibration curve $p_0(\rho)$, and then $r = ep_0/G$. By our previous experience based on a large number of lightly-doped p-Si samples ($p_0 \leq 2x10^{14}$ cm$^{-3}$), $r$ was found to be scattered from 0.6 to 0.7. In the two presently measured non-compensated samples, 72nc and 73nc – of essentially higher $p_0$ - the value of $r$ is significantly smaller: 0.46 and 0.38, resp. For the two compensated samples, 45c and 44c, we have determined the room-temperature value of $r$ (0.3 and 0.25, resp.) using the measured values of the Hall coefficient $G$ and the reported [3] values of $p_0$ (determined by a light reflection technique). The conversion of $G(T)$ into $p(T)$ was
performed neglecting a temperature dependence of \( r \). The deduced \( p(T) \) function, for the compensated sample 44c, is shown in Fig.1. The thick solid curve is the best fit to the experimental points, by the theoretical \( p(T) \) function [7] that is specified by the neutrality equation:

\[
p + N_a = N_a^0 = N_a p_a / (p_a + p)
\]

(1)

The fraction \( N_a^+/N_a \) of charged boron acceptors is controlled by a position of the Fermi level with respect to \( E_a \), or equivalently by the ratio of the hole concentration \( p \) and the characteristic hole concentration \( p_a(T) \) defined [6] through \( E_a \):

\[
p_a = g N_v \exp(- (E_a - E_v)/kT)
\]

(2)

Here \( N_v \) is the effective state density in the valence band (proportional to \( T^{3/2} \)), and \( g \) is the level degeneracy factor known to be 0.25 for shallow acceptors in Si.

The solution of Eq.(1) is strongly sensitive to the compensation degree \( N_d/N_a \) and hence both \( N_a \) and \( N_d \) can be extracted, by fitting, with a good precision. The deduced compensation degree is \( N_d/N_a = 0.41 \). To demonstrate a sensitivity of the \( p(T) \) curve to \( N_d/N_a \), two other theoretical \( p(T) \) curves, one for a smaller \( N_d/N_a = 0.2 \) (curve 2) and \( N_d/N_a = 0.6 \) (curve 3), are also shown in Fig.1. A reason for a sensitivity of the curve shape to \( N_d/N_a \) is as follows. At a fixed \( p_0 = N_a^0 - N_d \), a decrease in \( T \) results in the same downward shift of the Fermi level, and in the same reduction in the fraction \( N_a^+/N_a \) of charged acceptors, independent of the compensation degree. A reduction in the net charge, \( p = N_a^+ - N_d \), is then more pronounced in a compensated material, where \( N_a \) and \( N_d \) are comparable.

The BP pairs, if they exist at all, are inactive (neutral) defects that do not contribute into the neutrality equation (1) and hence do not affect the \( p(T) \) dependence.

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Fig.1 The hole concentration, by the Hall effect, for the compensated sample 44c (open circles). The thick solid curve 1 is computed with the best-fit values of \( N_a \) and \( N_d \) \( (N_d/N_a = 0.41) \). The thin solid curves are computed with a different compensation degree: \( N_d/N_a = 0.2 \) (curve 2) and \( N_d/N_a = 0.6 \) (curve 3).

Fig.2 The hole concentration deduced from the Hall effect in compensated sample 45c (curve 1) and non-compensated one 72nc (curve 2). The solid curves are computed with the best-fit values of \( N_a \) and \( N_d \); for 45c they are shown in Table 1, for 72nc they are \( N_a = 1.6x10^{16} \) cm\(^{-3} \), \( N_d = 7.8x10^{14} \) cm\(^{-3} \).
A difference in the temperature dependence of \( p(T) \), between a compensated sample and a non-compensated one, is further illustrated in Fig. 2 where results for the two moderately doped samples (45c and 72nc) are shown.

The deduced (best-fit) acceptor concentration \( N_a \) and the donor concentration \( N_d \) in the two compensated samples are compared, in Table I, with the reported [3] hole concentration \( p_0 \) and the total impurity concentrations \( N_B \) and \( N_P \) (of boron and phosphorus, resp.). There is some difference between \( N_a \) and \( N_B \) and between \( N_d \) and \( N_P \), but this can be attributed to some inaccuracy in the concentrations, rather than to B-P pairing. The most important finding is that there is indeed a significant difference between the hole concentration \( p_0 \) and the concentration \( N_a \) of isolated boron acceptors.

Table I Parameters of compensated samples: \( N_a \) and \( N_d \) as deduced in the present work; the other quantities - as reported in ref. [3]

<table>
<thead>
<tr>
<th>Sample</th>
<th>( p_0 ) (cm(^{-3}))</th>
<th>( N_a ) (cm(^{-3}))</th>
<th>( N_d ) (cm(^{-3}))</th>
<th>( N_B ) (cm(^{-3}))</th>
<th>( N_P ) (cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>45c</td>
<td>( 1 \times 10^{16} )</td>
<td>( 2.3 \times 10^{16} )</td>
<td>( 1.3 \times 10^{16} )</td>
<td>( 3.7 \times 10^{16} )</td>
<td>( 3.3 \times 10^{16} )</td>
</tr>
<tr>
<td>44c</td>
<td>( 3.6 \times 10^{16} )</td>
<td>( 7 \times 10^{16} )</td>
<td>( 3 \times 10^{16} )</td>
<td>( 7.1 \times 10^{16} )</td>
<td>( 4.5 \times 10^{16} )</td>
</tr>
</tbody>
</table>

4. Summary

The concentrations \( N_a \) (of isolated boron acceptors) and \( N_d \) (of isolated phosphorus donors) were deduced from the temperature dependence of the Hall effect, for the compensated and reference samples that were previously used [3, 6] to trace the lifetime degradation. It has been confirmed that \( N_a \) and \( N_d \) are comparable in the compensated (co-doped) samples, which implies that a suspected B-P pairing is actually insignificant, and accordingly the room-temperature hole concentration \( p_0 \) is essentially smaller than \( N_a \).

Fig. 3 Reported saturated degradation \( R_s \) plotted in dependence of (a) concentration \( N_a \) of isolated boron acceptors, (b) room-temperature hole concentration \( p_0 \). The filled circles correspond to the two compensated samples (44c and 45c), the open circles – to the two non-compensated samples (72nc and 73nc), the triangle – to the data previously reported [2] for boron-only doped samples.
A reported correlation [3] of the lifetime degradation with $p_0$ implies a lack of correlation with $N_a$. To illustrate
this statement, the degradation amplitude $R_s$ – which is a saturated increment in the reciprocal electron lifetime - is
plotted in Fig.3a as a function of $N_a$. For the two compensated samples, marked by filled circles, our values for $N_a$
(Table 1) are used. For non-compensated samples, marked by open circles, $N_a$ is identical to $p_0$, and obtained from
the measured room-temperature resistivity. Beside the four presently inspected samples, also the data for previously
studied [2] only-boron doped samples, of comparable oxygen concentration, are shown.

In Fig. 3b, $R_s$ is plotted in dependence of $p_0$, for the same samples. The two plots of Fig.3 clearly show that $R_s$
correlates with $p_0$ but not with $N_a$.

This conclusion supports a recently proposed mechanism [4] of degradation based on grown-in $\text{B}_2\text{O}_3$ defects - of a
concentration proportional to $p_0$ and not to $N_a$.

5. References