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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 Bs 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 (τ) 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, $R(t) = 1/\tau(t) - 1/\tau(0)$, 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_sO_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_s 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_d of isolated phosphorus donors is much smaller than the total phosphorus concentration N_P, and accordingly the concentration N_a of isolated boron acceptors remains close to p, in spite of co-doping. In this case the proportionality of R_s to the concentration N_a 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_a of isolated boron acceptors is actually close to the total boron concentration N_B (and the concentration N_d of isolated phosphorus donors is close to the total phosphorus concentration N_P). In that case the hole concentration, $p = N_a – N_d$, is essentially smaller than N_a, in compensated samples. Hence, a proportionality of the degradation amplitude R_s to p implies that R_s does not correlate with N_a. Such a behaviour is not consistent with a B_sO_2 model of the degrading centre, but it can be accounted for within an advanced model [4] based on formation of single-positive B_iO_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 B_iO_2 defects will follow a pC^2 dependence, and not an N_aC^2 dependence. The grown-in B_iO_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 B_iO_2 (denoted SRC) that is recombination-active.

The foundation of the new model is an essential difference between p and N_a 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_a and N_d 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 ρ 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_a and N_d.

3. Results

The measured Hall coefficient $G(T)$ is related to the hole concentration $p(T)$ by $G = r/(ep)$, 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 ρ: the resistivity ρ 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 ($p_0 \leq 2x10^{15}$ 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:

$$p + N_d = N_a^- = N_a p_a / (p_a + p) \quad . \tag{1}$$

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:

$$p_a = g N_v \exp(-(E_a - E_v)/kT) \quad . \tag{2}$$

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.

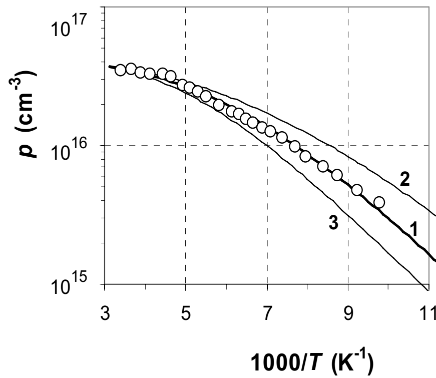

Fig.1 The hole concentration, by the Hall effect, for the compensated sample 44c (open circles). The thick solid curve 1 is computed with the best-fit values of N_a and N_d (N_d/N_a = 0.41). The thin solid curves are computed with a different compensation degree: N_d/N_a = 0.2 (curve 2) and N_d/N_a =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

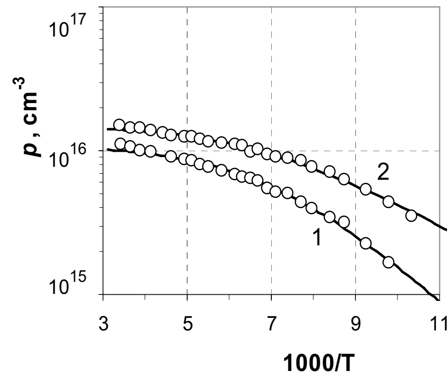

Fig.2 The hole concentration deduced from the Hall effect in compensated sample 45c (curve 1) and non-compensated one 72nc (curve 2). The solid curves are computed with the best-fit values of N_a and N_d; for 45c they are shown in Table 1, for 72nc they are $N_a = 1.6 \times 10^{16}$ cm^{-3}, $N_d = 7.8 \times 10^{14}$ cm^{-3}.

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.

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 $N_d/N_a = 0.4$ (curve 2) and the other for a larger $N_d/N_a = 0.6$ (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 $p_0 = N_a - N_d$, 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.

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_o 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]

Sample	p_0, cm^{-3}	N_a, cm^{-3}	N_d, cm^{-3}	N_B, cm^{-3}	N_P, cm^{-3}
45c	10^{16}	$2.3x10^{16}$	$1.3x10^{16}$	$3.7x10^{16}$	$3.3x10^{16}$
44c	$3.6x10^{16}$	$7x10^{16}$	$3x10^{16}$	$7.1x10^{16}$	$4.5x10^{16}$

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.

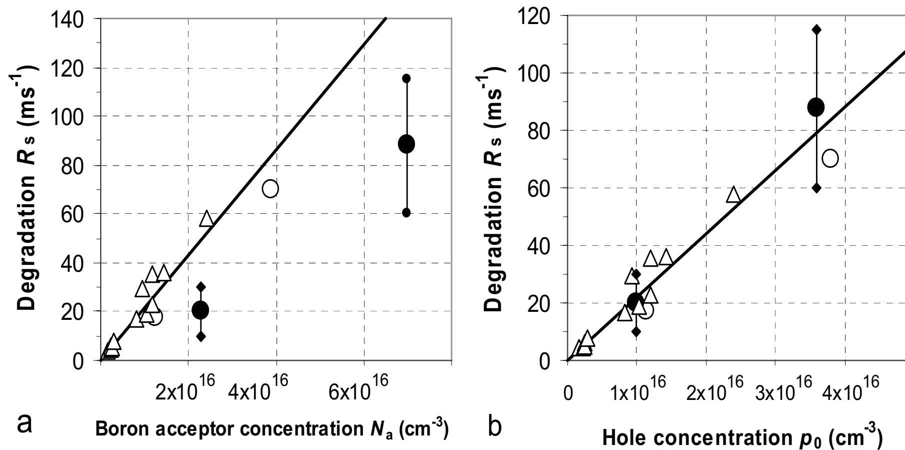

Fig.3 Reported saturated degradation R_s plotted in dependence of (a) concentration N_a of isolated boron acceptors, (b) room-temperature hole concentration p_0. The filled circles correspond to the two compensated samples (44c and 45c), the open circles – to the two non-compensated samples (72nc and 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 B_iO_2 defects - of a concentration proportional to p_0 and not to N_a.

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