MODELING THE GENERATION AND DISSOCIATION OF THE BORON-OXYGEN COMPLEX IN B-DOPED CZ-SI

Bianca Lim, Karsten Bothe, and Jan Schmidt
Institut für Solarenergieforschung Hameln (ISFH), Am Ohrberg 1, 31860 Emmerthal, Germany

ABSTRACT

We demonstrate that the boron-oxygen (B_sO_{2i}) recombination center responsible for the light-induced degradation of Czochralski silicon solar cells can be deactivated by simultaneous annealing and illumination. After applying this deactivation treatment the improved carrier lifetime is shown to be stable under illumination at room temperature. The measured dependence of the deactivation rate as a function of temperature indicates that the process is thermally activated. Based on the experimental findings a defect reaction model is proposed which attributes the deactivation to a dissociation reaction of a complex XY of unknown composition and to the subsequent association of one component X of this complex with the oxygen dimer O_{2i} into XO_{2i}, thereby reducing the concentration of unbound O_{2i}. An excellent agreement between the experimental and the modeled time dependence of the B_sO_{2i} concentration is found.

INTRODUCTION

It is well known that the efficiency of solar cells made on boron-doped Czochralski-grown silicon (Cz-Si) degrades under illumination at room temperature until a stable saturation level is reached [1,2]. The reason for this degradation has recently been identified to be the formation of a defect complex B_sO_{2i} consisting of one substitutional boron atom (B_s) and one interstitial oxygen dimer (O_{2i}) [3]. This boron-oxygen recombination center has been found to ultimately limit the carrier lifetime of B-doped Cz-Si [4]. A complete reversal of this lifetime degradation can be achieved by annealing in the dark at ~200 °C for 10 min, however, subsequent illumination at room temperature completely degrades the lifetime again [5]. More recently, it was demonstrated by Herguth et al. [6,7] that the illumination of B-doped Cz-Si solar cells at elevated temperature (70 – 160 °C) results in a nearly complete recovery of the boron-oxygen-related degradation, which is stable under illumination at room temperature for more than 140 h. After an initial degradation of the open-circuit voltage of a Cz-Si solar cell under illumination at 70 °C a subsequent increase to 80 % of the initial open-circuit voltage was observed [6,7]. Since the open-circuit voltage of a solar cell correlates with its bulk carrier lifetime, it was concluded that the bulk carrier lifetime almost completely recovers if excess carriers are present at elevated temperatures. However, no model capable of explaining the observed defect deactivation was proposed.

In this contribution, we confirm by means of direct measurements of recombination lifetimes that high and stable lifetimes can be achieved in B-doped Cz-Si wafers by simultaneously annealing and illuminating them. Based on the experimental results, a defect reaction model is developed, which is capable of explaining the observed deactivation effect.

LIFETIME MEASUREMENTS

The material used in this study is 1.4-Ωcm B-doped Cz-Si with a thickness of 300 µm and an interstitial oxygen concentration of $[O_i] = (7.5\pm0.5)\times10^{17}$ cm^{-3}, as determined by means of Fourier transform infrared spectroscopy. Sample preparation includes an acidic damage etch, an RCA cleaning, and a PECVD silicon nitride surface passivation [8] on both sides of each sample. In addition, a ~100 Ω/sq phosphorus (P) diffusion is performed at 847 °C for half the samples on both wafer surfaces. The resulting n^+ layers on both wafer sides are removed by a second acidic etch prior to the silicon nitride deposition. The phosphorus diffusion serves two purposes: (i) metallic impurities are effectively removed from the silicon bulk by gettering and (ii) the maximum B_sO_{2i} concentration is reduced by a factor of 2-3 [9]. Lifetime measurements are performed at 300 K using the quasi-steady-state photoconductance (QSSPC) technique [10], which allows the extraction of lifetimes at a well-defined injection density. In order to start from a defined state, all samples are either annealed in the dark for 10 min at 200 °C or illuminated at room temperature at a light intensity of 50 mW/cm^2 for more than 12 h before we begin to monitor the lifetime. Accordingly, most of the boron-oxygen complexes are expected to be either completely dissociated or generated when the samples are placed on a hotplate and illuminated at 70 mW/cm^2 with a halogen lamp, the light intensity of which is determined using a calibrated solar cell. Since the QSSPC measurements are all performed at room temperature, the samples are temporarily removed from the hotplate for short time intervals of approximately 60 s. To test the stability of the lifetime after the deactivation of the B_sO_{2i} recombination center, the samples which were illuminated at 408 K are removed from the hotplate after 140 h and are then illuminated at 50 mW/cm^2 for more than 150 h at room temperature (300 K). During that time the lifetime is stable within the uncertainty range of the QSSPC measurement, which is approximately ±10 %, as can be seen from Fig. 1.

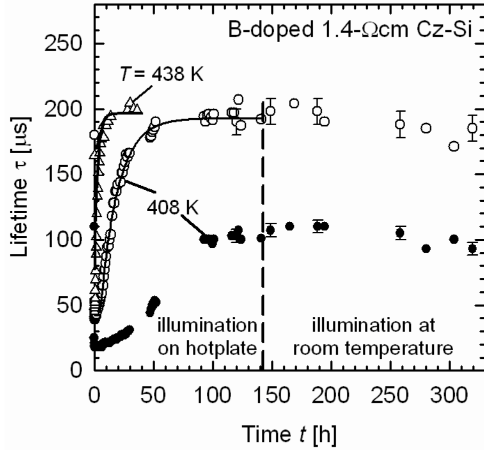

FIG. 1. Time dependence of the lifetime τ of two P-diffused (open symbols) and one undiffused (closed circles) Cz-Si samples which are illuminated at 135 °C and 165 °C, respectively, at a light intensity of 70 mW/cm^2. The solid lines represent fits of an exponential rise to maximum function, which yield the time constants τ_{de} of the deactivation process.

Performing deactivation experiments of the type shown in Fig. 1 at different temperatures in the range bet ween 408 and 485 K shows that the deactivation process is thermally activated. Figure 2 shows the deactivation rate $R_{de} \equiv 1/\tau_{de}$ obtained from the exponential fits to the time-dependent lifetime curves as a function of inverse temperature $1000/T$. Up to the maximum temperature of 485 K the measured $R_{de}(1/T)$ dependence can be fitted by an Arrhenius law

$$R_{de} = \nu_0 \exp(-E_{de}/kT), \tag{1}$$

where ν_0 is the attempt frequency and E_{de} is the activation energy of the deactivation process. For the phosphorus-diffused samples the fit in Fig. 2 yields $E_{de.P} = (0.72 \pm 0.07)$ eV and $\nu_{0.P} = (2.0 \pm 0.5) \times 10^4$ s^{-1}. For the undiffused Cz-Si samples a similar E_{de} of (0.69±0.06) eV is obtained, however, the attempt frequency is one order of magnitude lower: $\nu_0 = (4 \pm 2) \times 10^3$ s^{-1}.

THEORETICAL MODEL

Based on the experimental results shown in Figs. 1 and 2 we introduce a defect reaction model which is capable of explaining the complete time evolution of the carrier lifetime as shown in Fig. 1. Assuming that the only recombination-active defect formed or disappearing during illumination in B-doped Cz-Si is the B_sO_{2i} complex, the normalized defect concentration N_t^*, which is defined as the difference between the inverse lifetime after a period t of illumination $\tau^{-1}(t)$ and the inverse lifetime before illumination τ_0^{-1}, is proportional to the B_sO_{2i} concentration, i.e. $N_t^* = \tau^{-1}(t) - \tau_0^{-1} \propto [B_sO_{2i}]$. As has been shown in previous publications [3,11], the initial lifetime degradation observed during the first few minutes of illumination can be

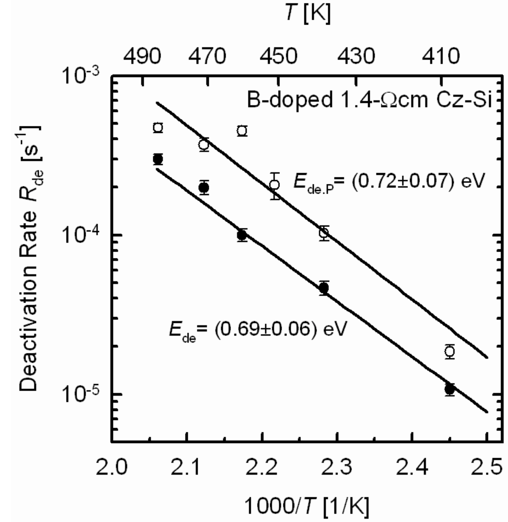

FIG. 2. Arrhenius plot of the deactivation rate R_{de} for the same samples as shown in Fig. 1. The illumination intensity during the deactivation is set at 70 mW/cm^2. The Arrhenius fits give activation energies of $E_{de.P} = (0.72 \pm 0.04)$ eV and $E_{de} = (0.69 \pm 0.06)$ eV for the P-diffused and the undiffused Cz-Si samples, respectively.

explained by a recombination-enhanced defect reaction of a fast-diffusing oxygen dimer O_{2i} and an immobile substitutional boron atom B_s:

$$B_s + O_{2i} \rightleftharpoons B_sO_{2i} \tag{2a}$$

where the generation and dissociation rates of the B_sO_{2i} complex R_{a1} and R_{d1} have been experimentally determined with a high degree of accuracy [12]. In order to be able to model the lifetime recovery, a side defect reaction involving a complex XY of unknown composition is introduced. XY dissociates by a recombination-enhanced reaction into its components X and Y and one of the components, e.g. X, forms a complex XO_{2i} with the highly mobile oxygen dimer, leading to the reactions:

$$XY \rightleftharpoons X + Y \quad \text{and} \tag{2b}$$

$$X + O_{2i} \rightleftharpoons XO_{2i} \tag{2c}$$

In this model, the time dependence of the lifetime depicted in Fig. 1 can be understood as follows: Initially, all oxygen dimers O_{2i} are free while species X is bound in the complex XY. Due to the recombination-enhanced diffusion of the oxygen dimers, B_sO_{2i} centers form very fast under illumination, while the complex XY, assuming a slow XY dissociation, gradually begins to dissolve. Accordingly, reaction (2a) will be in equilibrium after a short period and the fraction of unbound O_{2i} begins to react with the emerging species X to form the recombination-inactive complex XO_{2i}. Reaction (2a) then requires that more B_sO_{2i} complexes dissociate to conserve the (quasi)-equilibrium state. Hence, the number of recombination-active B_sO_{2i} centers is reduced.

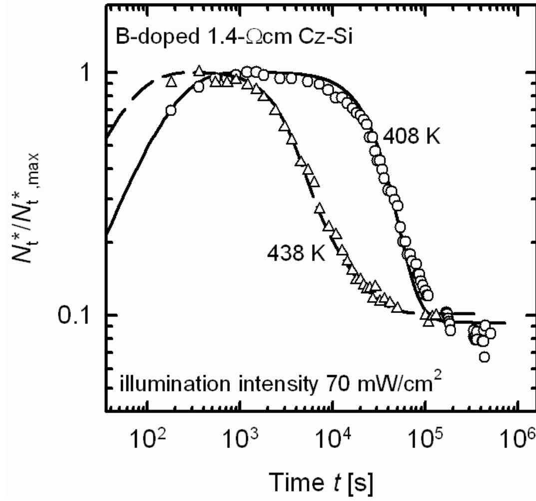

FIG. 3. Measured (symbols) and calculated (lines) time dependence of the normalized defect concentration N_t^* obtained from the data of the P-diffused samples shown in Fig. 1 at two different temperatures (135 and 165 °C).

To experimentally verify this model, the time-dependent concentration of the B_sO_{2i} defect center deduced from the model has to be compared to experimental data, which in turn requires the solution of the corresponding rate equations. However, since the three reactions (2) all happen simultaneously, the rate equations of the seven involved compounds are interdependent. In order to simplify the problem, two assumptions are made:

(i) the concentration of substitutional boron $[B_s]$, which equals the doping concentration N_{dop}, is much larger than the concentration of oxygen dimers $[O_{2i}]$, and

(ii) the concentration of the species Y, i.e. [Y], is much larger than the concentration of the species X, i.e. [X].

Hence, $[B_s] = N_{dop}$ and [Y] can be assumed to be time-independent and two of the seven rate equations can be neglected. The five remaining rate equations are:

$$d[B_sO_{2i}]/dt = - k_{d1} [B_sO_{2i}] + k_{a1} [B_s] [O_{2i}], \quad (3a)$$

$$d[XY]/dt = - k_{d2} [XY] + k_{a2} [X] [Y], \quad (3b)$$

$$d[XO_{2i}]/dt = - k_{d3} [XO_{2i}] + k_{a3} [X] [O_{2i}], \quad (3c)$$

$$d[O_{2i}]/dt = k_{d1} [B_sO_{2i}] - k_{a1} [B_s] [O_{2i}] + k_{d3} [XO_{2i}] - k_{a3} [X] [O_{2i}], \quad (3d)$$

$$d[X]/dt = k_{d2} [XY] - k_{a2} [X] [Y] + k_{d3} [XO_{2i}] - k_{a3} [X] [O_{2i}], \quad (3e)$$

where k_{di} and k_{ai} are the dissociation and association rate constants, respectively [13]. Note that $k_{d1} = R_{d1}$ and $k_{a1}N_{dop} = R_{a1}$ where R_{d1} and R_{a1} are the dissociation and association rates for the B_sO_{2i} complex reported in the literature [12]. Figure 3 depicts measured data (symbols) of

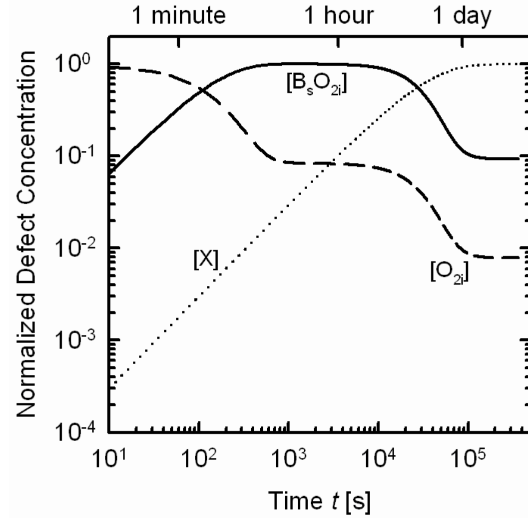

Fig 4. Simulated time dependence of the concentrations of the boron-oxygen center (B_sO_{2i}), free oxygen-dimers (O_{2i}) and the compound X. All concentrations are normalized to their maximum values.

the normalized defect concentration N_t^* divided by the maximum defect concentration $N_{t,max}^*$, which was derived from the lifetime data shown in Fig. 1. In addition, Fig. 3 also shows theoretically calculated data (lines) for the normalized concentration of the boron-oxygen complex $[B_sO_{2i}]/[B_sO_{2i}]_{max}$. The calculation is done iteratively for all time-dependent concentrations in Eq. (3) by converting the differential equations into difference equations and assuming that at $t = 0$, $[B_sO_{2i}] = 0$, $[O_{2i}] = N_{t,max}^*$, $[X] = 0$, and $[XO_{2i}] = 0$. Furthermore, [XY] was set at a constant value. As can be seen, an excellent agreement between theory and experiment is obtained.

An example of such a calculation is shown in Fig. 4. At first, the concentration of the B_sO_{2i} complex increases, causing the concentration of oxygen-dimers to decrease. After a few minutes, both the B_sO_{2i} and the O_{2i} concentration saturate, indicating that Eq. (2a) has reached quasi-equilibrium. Meanwhile, the complex XY slowly dissociates, resulting in an increase of the concentration of X. Once [X] has reached a critical level, free oxygen-dimers and free X also begin to form the complex XO_{2i}. At this point, boron-oxygen complexes begin to dissociate to retain the quasi-equilibrium of Eq. (2a) and the concentration of B_sO_{2i} accordingly decreases. This continues until the majority of oxygen-dimers is bound in the complex XO_{2i}, at which point all three concentrations begin to saturate. In this calculation, which corresponds to the experimental data of the P-diffused sample regenerated at 135 °C, the final number of recombination-active boron-oxygen complexes was decreased by one order of magnitude.

Importantly, the proposed model is also capable of explaining the increased deactivation rate R_{de} with increasing temperature T. Considering Eq. (3c), the generation of the complex XO_{2i} depends on the amount of available X and O_{2i} as well as the generation rate k_{a3}. Hence,

both an increase of k_{a3} and/or a higher dissociation rate of the complex XY, i.e. k_{d2}, will lead to a more rapid dissociation of the B_sO_{2i} complexes. As mentioned above, the deactivation rate is also increased by the phosphorus diffusion step. Deactivation of the B_sO_{2i} complex in an as-grown sample takes up to three times longer than in a sample which was P-diffused. With regard to the proposed defect reaction model, a possible explanation for this difference could be a speeding up of the XY dissociation due to the increase of one or both components of the XY defect during the high-temperature phosphorus diffusion process.

CONCLUSIONS

In this study, it was shown that the light-induced boron-oxygen-related recombination center in Cz-Si can be deactivated by simultaneously illuminating the silicon wafer with white light and annealing it at temperatures between 135 and 210 °C. The deactivation process was shown to be thermally activated with an activation energy of 0.7 eV. The recombination lifetime after deactivation was found to be stable under illumination at room temperature. Based on the experimental findings, we have proposed a defect reaction model which is capable of explaining the deactivation process.

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