FORMATION AND ANNIHILATION OF THE METASTABLE DEFECT IN BORON-DOPED CZOCHRALSKI SILICON

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ABSTRACT

This paper aims at elucidating the physical mechanism responsible for the light-induced efficiency degradation of solar cells fabricated on boron-doped Czochralski silicon (Cz-Si). Lifetime measurements on Cz-Si wafers at defined injection levels show that the concentration of the light-induced metastable defect increases *linearly* with the substitutional boron concentration. Moreover, a *quadratic* increase with the interstitial oxygen density is measured. The defect generation rate is examined as a function of temperature at constant illumination intensity. Our measurements clearly prove that the defect generation process is thermally activated with a relatively low energy barrier of $E_{gen} = 0.4$ eV. The activation energy of the defect annihilation process is determined to be independent of the boron doping level at $E_{ann} = 1.8$ eV. On the basis of our experimental findings, we introduce a new defect reaction model. In this model, fast-diffusing oxygen dimers O_{2i} are captured by substitutional boron B_s to form a complex B_s-O_{2i}, acting as highly effective recombination center. Promising new strategies for an effective reduction of the light degradation are derived from the proposed model.

INTRODUCTION

One of the major problems of solar cells fabricated on boron-doped Czochralski silicon (Cz-Si) is that their initial efficiency degrades under illumination until a stable performance level, typically 1-2% (absolute) below the initial efficiency, is reached. This fundamental effect, known for almost thirty years [1], is due to the degradation of the bulk carrier lifetime in the boron-doped Cz-Si base material. Despite its long history, a conclusive explanation of the effect is still to be found. The main difficulty in the past might have been the distinction between the fundamental effect (which is now known to be also present in boron-doped Cz-Si of highest purity) and metal-impurity related degradation effects like the dissociation of the iron-boron pair [2]. Only five years ago Schmidt et al. [3] proposed the first metal-impurity free defect reaction model capable of explaining the fundamental lifetime degradation effect as well as the characteristic recovery behavior during annealing at low temperature. In this model, a lifetime-reducing recombination center made up of one interstitial boron and one interstitial oxygen atom B_iO_i is created under illumination (large concentrations of oxygen are practically unavoidable in Cz-Si due to the partial dissolution of the silica crucible during the growth process). Interestingly,

it was found that gallium-doped and phosphorus-doped Cz silicon as well as oxygen-free float-zone silicon samples do not present any lifetime degradation effect, which is thus exclusively linked to the simultaneous presence of boron and oxygen in the material [3,4]. According to the theoretical considerations of Ohshita et al. [5], the B_iO_i pair could only exist in a stable configuration if a substitutional silicon atom is sited between the boron and the oxygen atom.

Glunz et al. [6] verified the strong correlation between the light-induced lifetime degradation in Cz-Si and the boron as well as the oxygen concentration. However, whereas they found an approximately linear increase of the lifetime degradation with boron doping concentration, a strongly superlinear increase with interstitial oxygen concentration, approximately to the power of five, was observed. These results gave rise to the suspicion that the Cz-specific recombination center is probably associated with a defect complex different from the B_iO_i pair. Moreover, it is highly doubtful if any interstitial boron exists in non-particle-irradiated silicon at all. These considerations were further supported by measurements of Schmidt and Cuevas [7] using injection-level dependent lifetime spectroscopy (IDLS). They showed that the energy level of the light-induced recombination center is very different from that of the B_iO_i pair and proposed a new core structure consisting of one substitutional boron B_s and several oxygen atoms. More recently, Bourgoin et al. [8] proposed a possible atomic configuration of the boron-oxygen complex where the B_s atom is surrounded by three O_i atoms. They also suggested a new degradation mechanism where electron trapping induces a Jahn-Teller distortion, shifting one of the energy levels of the defect to midgap. However, an experimental verification of the proposed mechanism was not performed.

In this paper, we introduce a new defect reaction model, based on fast-diffusing oxygen dimers. The model is fully consistent with all our experimental data and allows us to derive new possible remedies for the light-induced degradation.

IMPACT OF BORON AND OXYGEN

In order to clarify the core structure of the metastable boron- and oxygen-related defect in Cz-Si, we have analyzed the normalized defect concentration $N_t^* \equiv 1/\tau_d - 1/\tau_0$ as a function of the interstitial oxygen concentration $[O_i]$ and the substitutional boron concentration $[B_s]$. Using the
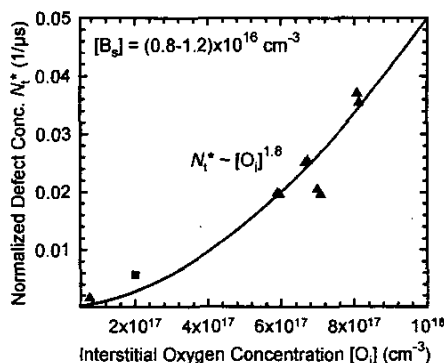
Fig. 1. Measured normalized defect concentration N_t^* as a function of the interstitial oxygen concentration $[O_i]$ for several Cz-Si samples (triangles) and one mc-Si wafer (square). The boron concentrations are very similar $[B_s]$ = $(0.8-1.2)\times10^{16}$ cm^{-3}. The solid line is fitted to the measured data and follows a power law $N_t^*\sim[O_i]^{1.8}$.

quasi-steady-state photoconductance (QSSPC) technique [9], the effective carrier lifetimes were measured before (τ_0) and after (τ_d) light degradation at a constant, well-defined injection level Δn.

Figure 1 shows the normalized defect concentration N_t^*, measured at a constant injection level of Δn = 1×10^{15} cm^{-3}, as a function of the interstitial oxygen concentration $[O_i]$. The boron concentration, as determined from resistivity measurements, is approximately the same for all samples $[B_s]=(0.8-1.2)\times10^{16}$ cm^{-3}. The interstitial oxygen concentration was determined according to DIN 50438-1 using a Bruker Equinox 55 FTIR spectrometer. Both surfaces of each wafer were passivated by means of PECVD silicon nitride films, resulting in a very low surface recombination velocity below 10 cm/s. As has been verified on float-zone silicon wafers, the surface passivation quality does neither change during light soaking nor during low-temperature annealing. In Fig. 1, all data measured on Cz-grown silicon samples are represented by triangles. The very low O_i
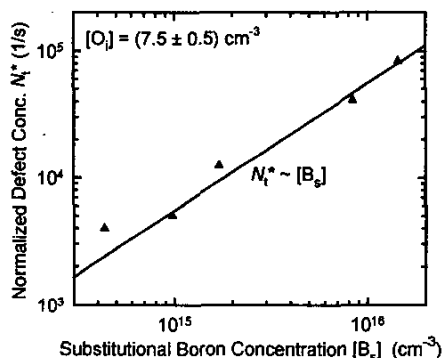

Fig. 2. Measured normalized defect concentration N_t^* as a function of the substitutional boron concentration $[B_s]$ for Cz-Si wafers with similar O_i concentrations $[O_i]$ = (7-8)$\times10^{17}$ cm^{-3} (symbols). The fitted line shows that N_t^* increases linearly with $[B_s]$.

concentration of 7.5×10^{16} cm^{-3} was achieved by applying a magnetic field during Cz crystal pulling. Also included in Fig. 1 is one phosphorous-gettered multicrystalline silicon (mc-Si) wafer (square) which shows the same light degradation behavior as the Cz samples. The most striking result of Fig.1 is the fact that we find an approximately *quadratic* increase of N_t^* with $[O_i]$, which is a much weaker dependence compared to that found in a recent study by Glunz et al. [6]. This discrepancy might partly be due to the different measurement conditions applied in both studies. While our lifetime data were measured at a fixed injection level, the measurements in [6] were performed at a constant bias light intensity, resulting in different injection levels for samples with varying lifetimes.

Figure 2 shows the measured dependence of N_t^* on $[B_s]$ for Cz-Si wafers with similar levels of oxygen contamination $[O_i]$ = (7-8)$\times10^{17}$ cm^{-3}. As the boron doping concentrations vary between 4×10^{14} and 1.4×10^{16} cm^{-3}, the lifetime data were not recorded at a fixed injection level but under low-injection conditions. In perfect agreement with [6,7], we find a *linear* increase of N_t^* with increasing $[B_s]$.

DEFECT GENERATION

In previous studies, a recombination-enhanced defect reaction was suggested as a possible mechanism for the defect formation in Cz-Si [3,10]. Recently, Rein et al. [11] demonstrated that the defect generation rate shows a quadratic dependence on the doping concentration. In addition, they found that the generation rate shows a negligible dependence on the injected carrier concentration. From these findings they concluded that the physical mechanism of the defect transformation is not a recombination-enhanced process.
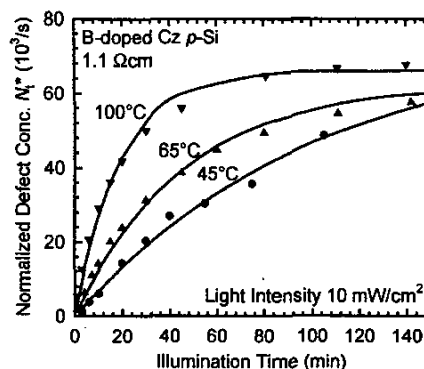

Fig. 3. Isothermal measurements of the time-dependent normalized defect concentration $N_t^*(t)$. Between each measurement, the sample was illuminated with a halogen lamp at 0.1 suns at temperatures ranging from 45 to 100°C.

In order to shed some light on the defect generation mechanism, we have examined the temperature dependence of the defect generation rate R_{gen}. Figure 3 shows isothermal measurements of the time-dependent normalized defect concentration $N_t^*(t)$ performed at a fixed injection level of Δn = 1×10^{15} cm^{-3}. Between each measure-

ment, the Cz-Si samples were illuminated with a halogen lamp at 0.1 suns at temperatures ranging from 45 to 100°C. In this temperature range, the defect annihilation can be neglected. As can be seen from Fig. 3, the rise time τ_{gen} of $N_t^*(t)$, and hence $R_{gen} = 1/\tau_{gen}$, depends strongly on temperature. $R_{gen}(T)$ was determined by fitting the function $N_t^*(t,T) = N_t^*(t\rightarrow\infty)$ [1 – exp($-R_{gen}(T)$ t)] to the measured data. The initial very fast decay of the carrier lifetime observed during the first few minutes of light soaking has not been analyzed here. Figure 4 shows a plot of R_{gen} as a function of inverse temperature $1/T$. The defect generation rate can be fitted using the equation

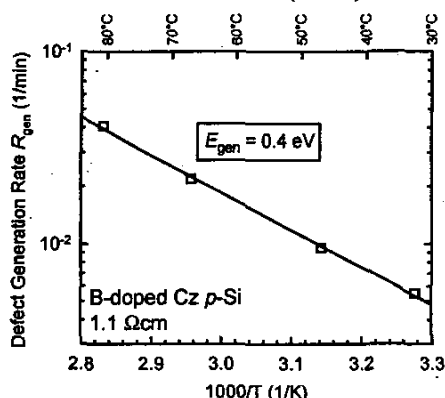$$R_{gen}(T) = R_{gen}(T \rightarrow \infty)\exp\left(-\frac{E_{gen}}{kT}\right) \qquad (1)$$

Fig. 4. Arrhenius plot of the defect generation rate R_{gen}. An activation energy of E_{gen} = 0.4 eV is obtained from the fit (line) to the measured data (squares).

Hence, our results clearly prove that the physical mechanism responsible for the light degradation of boron-doped Cz-Si solar cells is a *thermally activated* process with a relatively low activation energy of E_{gen} = 0.4 eV. This important finding points towards a diffusion-limited defect reaction.

DEFECT ANNIHILATION

The defect annihilation has been shown to be thermally activated as well [11]. In order to determine the activation energy E_{ann} of this process, we have recorded the isothermal annealing curves of boron-doped Cz-Si samples of varying resistivities. Between each lifetime measurement, the samples were annealed in complete darkness at temperatures ranging from 115 to 145°C. In contrast to the study of Rein et al. [11], we have performed the lifetime measurements at intermediate injection levels and not under low-injection conditions because Cz-specific trapping effects may severely hamper lifetime measurements at very low injection levels [12]. The temperature dependence of the defect annihilation rate $R_{ann}(T)$ was determined by fitting the function $N_t^*(t,T) = N_t^*(0)$ exp($-R_{ann}(T)$ t) to the measured data. The Arrhenius plot of the annihilation rate shown in Fig. 5 clearly confirms that the annihilation process is thermally activated. The activation energy of E_{ann} = 1.8 eV obtained for the annihilation
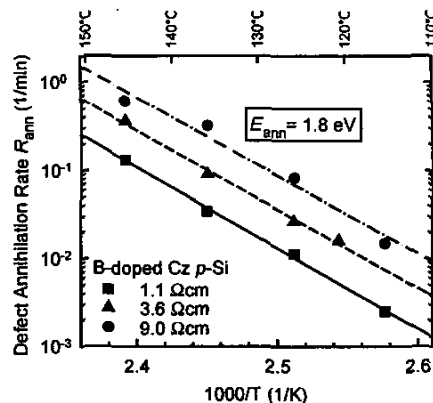

Fig. 5. Arrhenius plot of the defect annihilation rate R_{ann} for Cz-Si samples with different resistivities. The same activation energy of E_{ann} = 1.8 eV is obtained for all samples.

process does not depend on the doping concentration N_{dop} and is much larger compared to that of the defect generation process (E_{gen} = 0.4 eV). Even the lower E_{ann} value of 1.3 eV measured by Rein et al. [11] lies well above the barrier energy of the generation process. Another important finding of Fig. 5 is that R_{ann} *decreases* approximately *linearly* with N_{dop}. To our knowledge, this dependence has not been reported before.

DEFECT REACTION MODEL

Assuming the lifetime degradation in boron-doped Cz-Si is due to an actual defect reaction (and not due to a change of the defect configuration as proposed in Ref. [8]), the dependence of the metastable defect concentration N_t^* on [B_s] and [O_i] found in this study suggests that a reaction between a boron atom and a cluster of oxygen atoms takes place. As substitutional boron is largely immobile in the silicon lattice and interstitial boron exists only in negligible amounts in non-particle-irradiated silicon, we propose a new model where molecular oxygen is the mobile species in the defect reaction. As was first suggested by Gösele and Tan [13] , gas-like oxygen molecules, in particular the oxygen dimer O_{2i} which is made up of two O_i atoms, can be extremely fast diffusers in silicon. According to Ref. [13] the diffusivity of the oxygen dimer in silicon is approximately nine orders of magnitude higher than the diffusivity of interstitial atomic oxygen, because O_{2i} is only loosely coupled to the silicon lattice and no Si-O bonds have to be broken in the diffusion process. In our newly proposed defect reaction model, these O_{2i} molecules are captured by substitutional boron to form a B_s-O_{2i} complex which acts as a highly effective recombination center. The defect formation process is governed by the diffusion of the oxygen dimer and, hence, is a thermally activated process, which agrees well with our experimental findings. The role of the minority-carrier injection cannot be fully revealed on the basis of our experimental data. However, there are strong grounds for believing that the diffusivity of O_{2i} in silicon depends on its charge state, which may change under illumination or minority-carrier injection.
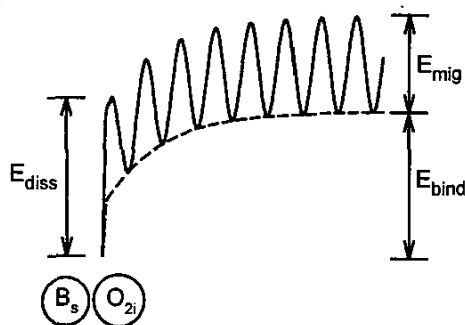
Fig. 6. Schematic energy diagram of the B_s-O_{2i} interaction

The formation and dissociation reaction of the proposed B_s-O_{2i} complex are determined by three characteristic energies shown in Fig. 6: the binding energy E_{bind}, the migration energy of the oxygen dimer E_{mig}, and the dissociation energy of the complex E_{diss}. E_{mig} has been calculated very recently by Lee et al. [14] on the basis of density-functional-theoretic total-energy calculations. In these calculations it was found that E_{mig} of the O_{2i} molecule in silicon lies between 0.3 and 1 eV, depending on the Fermi level position. For comparison, the migration energy of O_i in silicon is as high as 2.5 eV.

The migration energy in Fig. 6 corresponds to the activation energy of the defect generation process as determined above: $E_{mig} = E_{gen} = 0.4$ eV. This migration energy is much lower than that of O_i in silicon. Hence, we can exclude the participation of O_i in the boron-oxygen complex. However, $E_{mig} = 0.4$ eV is fully consistent with the migration energy range calculated by Lee et al. [14] for the oxygen dimer. The second characteristic energy determined from our measurements is the dissociation energy of the defect complex which corresponds to the activation energy of the defect annihilation process: $E_{diss} = E_{ann} = 1.8$ eV. Unfortunately, a direct calculation of E_{bind} from E_{diss} and E_{mig} is not possible (see Fig. 6).

The defect formation process suggested in this paper is similar to the thermal donor (TD) formation mechanism proposed by Gösele and Tan [13], where the O_{2i} molecules are captured by other oxygen atoms or clusters to form the different TDs. In fact, a detailed theoretical and experimental analysis [14,15] shows that during the first few hours of TD formation, the concentration of the O_{2i} dimer shows a pronounced decrease. As less O_{2i} molecules are available, we expect a decrease of the B_s-O_{2i} concentration and hence a reduced light degradation of the carrier lifetime after TD formation. In order to verify our hypothesis, we have annealed different boron-doped Cz-Si wafers at 450°C for up to 32 h. These conditions are ideal for the formation of TDs. After TD formation we measured a pronounced reduction of the metastable defect concentration up to a factor of three ! This experimental result is a nice indirect confirmation of our proposed model. Details of the long-term annealing experiments are given in a separate paper at this conference [16].

A second new method of reducing the light degradation could be the use of carbon-rich Cz-Si material. It is well known that the presence of carbon in a high concen-

tration suppresses TD generation in Cz-Si crystals. This phenomenon has recently been associated with the capture of oxygen dimers by substitutional carbon [17]. According to the model suggested in this paper, the C_s-O_{2i} formation is in direct competition with the formation of the lifetime-limiting B_s-O_{2i} defect complex. Hence, we expect a reduced lifetime degradation in Cz-Si wafers with high carbon content. Experimental tests of this promising new way of reducing the metastable defect concentration in boron-doped Cz-Si are currently under way in our lab.

CONCLUSIONS

Based on our experimental lifetime data, we have introduced a defect reaction model to describe the formation and annihilation kinetics of the metastable boron-oxygen-related defect complex in Cz-Si. In this model, fast migrating oxygen dimers O_{2i} are captured by immobile substitutional boron B_s to form the lifetime-limiting B_s-O_{2i} complex. Promising new strategies for an effective reduction of the light-induced degradation of Cz-Si solar cells have been derived from the proposed kinetic model.

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