Recombination-enhanced formation of the metastable boron–oxygen complex in crystalline silicon

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The formation process of the boron- and oxygen-related defect complex in crystalline silicon, responsible for the performance degradation of solar cells made on boron-doped Czochralski silicon (Cz–Si), is investigated on Cz–Si solar cells as a function of the applied voltage in the dark at temperatures ranging from 298 to 373 K. We show that the defect formation is not only a consequence of illumination or the application of a forward bias voltage but also occurs under equilibrium conditions at elevated temperatures in the dark. It can be partly suppressed by applying a reverse voltage. Our findings provide clear experimental evidence that a recombination-enhanced mechanism correlated with the total recombination rate is the driving force of the formation of the metastable defect. © 2003 American Institute of Physics. [DOI: 10.1063/1.1600837]

The efficiency of boron-doped Czochralski silicon (Cz–Si) solar cells decreases under illumination or minority-carrier injection in the dark by up to 10% relative.[1,2] This fact has its origin in the formation of a metastable recombination center related to the boron and oxygen content in the base material of the solar cell.[3–5] The formation of the boron–oxygen-related defect results in a pronounced decrease of the bulk carrier lifetime until a stable level is reached. A full recovery of the lifetime can be achieved by a short low-temperature anneal at temperatures above ~200 °C. Although the light-induced degradation was already discovered in 1973, a comprehensive understanding of the physical mechanisms is still to be found.[1] As the degradation not only occurs under illumination but also when minority carriers are injected in the dark, it had been concluded that the degradation is caused by excess charge carriers rather than directly by photons.[6] Another interesting recent finding showed that the defect formation rate does only weakly depend on the illumination intensity for intensities above 1 mW/cm^2.[7,8] However, it is noteworthy that even an illumination level of only 1 mW/cm^2 corresponds to a quasi-Fermi level splitting of several hundred millivolts and excess carrier concentrations in the vicinity of 10^{13} cm^{-3}. In order to verify the existence of a threshold value of the excess carrier concentration Δn at which the defect formation process starts, it is necessary to perform measurements at extremely low carrier densities. A well-defined method to do this is the injection of minority-carriers via a pn junction under forward bias. Using this method we analyze the dependence of the defect formation process on the applied voltage in detail and compare the results with numerical simulations and their predictions. Aiming to reduce the lack of understanding concerning the physics behind the formation of the metastable boron–oxygen complex, we discuss our results referring to recently proposed defect formation mechanisms.[5,8,9]

In order to study the defect formation process at a de-fined and reproducible excess carrier concentration, we apply a defined voltage to solar cells which we use as testing devices and measure the open-circuit voltage V_{oc} at fixed time intervals. The solar cells under investigation are 300-μm-thick metal–insulator–semiconductor (MIS)-contacted n^+p cells with an initial efficiency of ~19%. As substrate material 1.5 Ω cm boron-doped solar-grade Cz–Si with a typical interstitial oxygen content of 7×10^{17} cm^{-3} is used. The stable bulk carrier lifetime after cell processing is measured to be 30 μs at an injection level corresponding to one tenth of the doping concentration. The detailed processing sequence of this cell type has already been reported elsewhere.[10] From the measured V_{oc} values, the normalized metastable defect concentration $\tilde{N}_t$ is determined via

$$\tilde{N}_t(T,t,V_{appl}) = \frac{1}{\exp[qV_{oc}(T,t,V_{appl})/k_BT]} - \frac{1}{\exp[qV_{oc}(T,t=0,V_{appl})/k_BT]} \quad (1)$$

with V_{appl} being the applied voltage and k_B as the Boltzmann constant.[11] To adjust a defined initial state, the solar cells are annealed in the dark at 200 °C for 10 min before being placed on a preheated vacuum chuck covered by a black box in order to perform the forward-bias-induced degradation in complete darkness. While the box is opened manually for 2–3 s, the open-circuit voltage of the cell is measured at a light intensity of 10 mW/cm^2 using a halogen lamp located outside the box. This measurement procedure is repeated until no further degradation can be observed. For both the application of the forward bias voltage and the measurement of the open-circuit voltage, a four-quadrant operating source (Keithley 238) is used.

Figure 1 shows a set of typical degradation curves for different applied voltages V_{appl} at a constant temperature of 298 K. Depending on the applied voltage, different stable V_{oc} levels are reached. With increasing V_{appl} the stabilized V_{oc} value decreases, following a sigmoidal dependence.[12] Thus the application of a minimum voltage is necessary to initiate

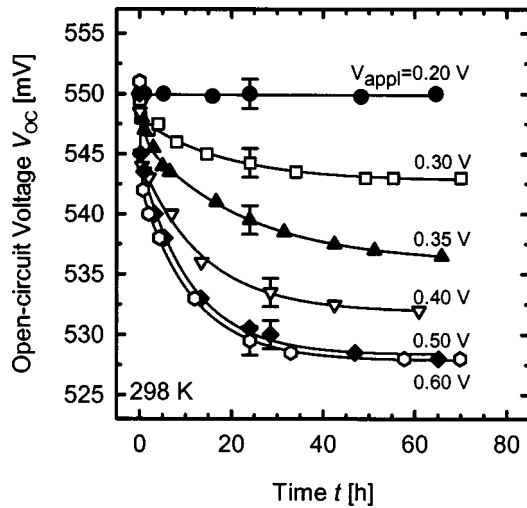[a]Electronic mail: k.bothe@isfh.de

FIG. 1. Forward-bias induced open-circuit voltage V_{oc} degradation curves of an MIS n^+p Cz–Si solar cell at different applied voltages V_{appl} measured at a temperature of $T=298$ K. During each measurement the solar cell is illuminated for 2–3 s with a halogen lamp of 10 mW/cm^2 intensity.

FIG. 3. Calculated dark minority-carrier densities n at half cell width of a high-efficiency silicon solar cell as a function of the applied voltage V_{appl}. The inset shows that in comparison to the case of no applied voltage, the dark electron density can be reduced by applying a reverse bias voltage.

the degradation process. For applied voltages above a certain value no further changes in the V_{oc} degradation curves are observed. The percentage of activated recombination centers after complete degradation as a function of the applied voltage is shown in Fig. 2 for different temperatures ranging from 298 to 373 K. With increasing temperature the degradation curve and therefore the threshold voltage $V_{appl. min}$ above which the degradation is observed is shifted to smaller voltages. Increasing the temperature from 300 to 350 K shifts $V_{appl. min}$ by almost 200 mV. Interestingly, for temperatures above 300 K the defect concentration does not decrease to zero and a pronounced degradation can be observed even in the case when no voltage is applied. This finding seems not to agree with the widely accepted opinion that the metastable boron–oxygen defect is only formed under nonequilibrium conditions, i.e., during illumination or the application of a forward bias voltage in the dark.

Using the device simulation program PC1D V5.1,[13] we have calculated the minority carrier density n at half cell thickness for different applied voltages and temperatures.
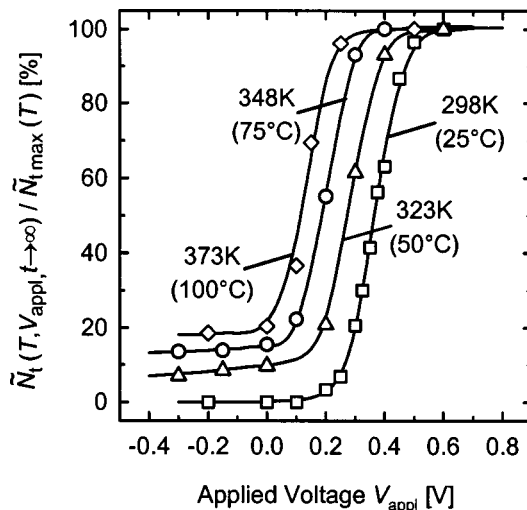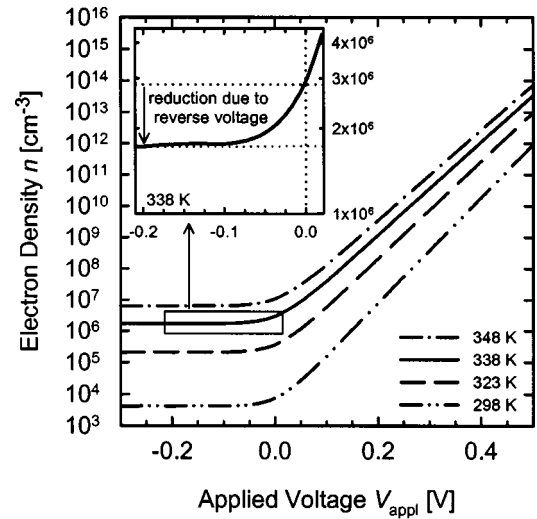
The solar cell parameters used for this simulations are identical to those used to calculate the impact of the light-induced recombination centers on the current-voltage characteristics of Cz silicon solar cells.[14] The results of the simulations are shown in Fig. 3. At 348 K in the dark and with no voltage applied, where a pronounced degradation in V_{oc} can be observed experimentally (see Fig. 2), the minority-carrier density is calculated to be as low as 1 $\times 10^7$ cm^{-3}. As shown in the inset of Fig. 3 for $T=338$ K, n can be reduced compared to the case of no applied voltage by applying a reverse voltage to the cell. Thus, in case the degradation depends on the total number of minority carriers it should be possible to suppress the degradation by applying a small reverse voltage. Indeed, we are able to confirm this prediction experimentally as shown in Fig. 4. The stabilized V_{oc} value at $V_{appl}=-0.30$ V lies well above the level reached when no voltage is applied and degrades further when the
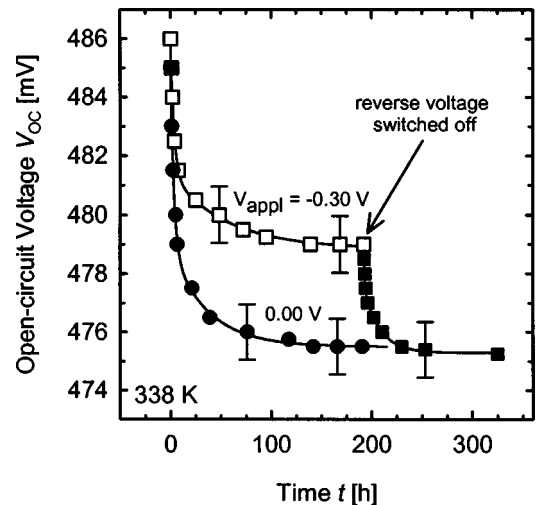

FIG. 2. Percentage of the activated recombination center depending on the applied voltage V_{appl} and the degradation temperature T.

FIG. 4. Measured effect of an applied reverse voltage V_{appl} on the degradation of the open-circuit voltage V_{oc} in the dark at 338 K for an MIS n^+p Cz–Si solar cell. Under equilibrium conditions with no voltage applied a pronounced degradation is present which can be partly suppressed by the application of a reverse-bias voltage.

reverse bias is switched off until the stable V_{oc} level corresponding to zero applied voltage is reached.

In recent studies, two fundamentally different mechanisms have been proposed for the activation of the metastable recombination center above a certain threshold voltage. The first mechanism attributes the activation of the center to a change of the charge-state occurring when the electron quasi-Fermi level shifts across the energy level of the center in its passive state.[5,8,9] In the second proposed mechanism it is assumed that the amount of energy required for the defect formation is supplied during a carrier recombination event (recombination-enhanced defect formation). Thus, an increase in the minority-carrier density, resulting in an increasing recombination rate, would enhance the defect formation. According to our experimental results shown in Fig. 2, we are able to exclude the first mechanism that predicts a shift of the curves corresponding to the change of the Fermi level with temperature. In the range of 300–350 K, the observed shift of $\sim$200 mV disagrees with the expected shift of 30 mV and therefore excludes this mechanism. However, the curves shown in Fig. 2 are fully consistent with the second mechanism described earlier. The defect formation starts at a certain recombination rate corresponding to a well defined minority-carrier threshold concentration. At high temperature, the minority-carrier concentration is higher than this threshold value even in the case of no applied voltage. Hence, the defect formation already takes place in case no or a reverse voltage is applied. Consequently, the high-temperature curves in Fig. 2 do not decrease to zero at low voltages. As can be seen from Fig. 3, the minority-carrier threshold density at which the degradation starts is around 3×10^6 cm^{-3} for the solar cells examined in this study. For an increased bias voltage the recombination rate increases and so does the saturation defect density. If the minority carrier concentration exceeds a certain level, a further increase in n does not result in a higher defect concentration, indicating that the maximum possible defect density is reached. This maximum value in the defect concentration is determined by the substitutional boron and interstitial oxygen concentration in the crystalline silicon material. Combining the results presented here with our recently proposed defect model for the metastable boron–oxygen complex we conclude that the formation of the defect takes place via a *recombination-enhanced diffusion process*.[15] The energy released during the recombination process is used to activate the di-oxygen complex (O_{2i}), consisting of two interstitial oxygen atoms at adjacent bond sites, which is captured by a substitutional boron atom (B_s), forming a B_s–O_{2i} defect complex being responsible for the performance degradation.[5]

In conclusion, we have shown that the formation of the metastable boron–oxygen complex in crystalline silicon is directly related to the *total* recombination rate and that the degradation already starts at extremely low minority-carrier concentrations. So far it was assumed that the *excess* charge carriers, i.e., the *net* recombination rate is the driving force of the defect formation. Our experimental results point towards a recombination-enhanced mechanism to be responsible for the defect formation, suggesting that the amount of energy released during a recombination event activates the diffusion of an oxygen dimer. The fast diffusing dimer is captured by substitutional boron to form the metastable boron–oxygen complex. This interpretation is also capable of explaining the surprising experimental finding that a lifetime degradation can be observed under equilibrium conditions (no voltage applied and complete darkness) at elevated temperatures ($>$300 K). For any fundamental experiment assuming equilibrium conditions, our result indicates a hitherto unaccounted source of inherent inaccuracy when using boron-doped Cz silicon.

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