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Lifetimes exceeding 1 ms in 1-Ω cm boron-doped Cz-silicon

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ABSTRACT

We perform carrier lifetime investigations on oxygen-rich boron-doped Czochralski-grown silicon (Cz-Si) wafers. As a characteristic feature of oxygen-rich boron-doped silicon materials, their lifetime is generally limited by boron–oxygen-related defects, intensifying their recombination-active properties under illumination or, more generally speaking, minority-carrier injection. In this study, we examine the following characteristic lifetime values of boron-doped Cz-Si: τ_0 after annealing in darkness (i.e. complete boron–oxygen defect deactivation), τ_d after illumination at room-temperature (i.e. in the completely degraded state) and τ_{0p} after illumination at elevated temperature (i.e. after 'permanent recovery'). We show that the permanent recovery process can be strongly influenced by a rapid thermal annealing (RTA) step performed in a conventional belt-firing furnace in advance of the permanent recovery process. We show that all measured lifetimes, i.e. τ_0, τ_d as well as τ_{0p}, are strongly influenced by the RTA process. We observe a strong increase of the lifetime after permanent recovery, depending critically on the RTA process parameters. On 1-Ω cm Cz-Si material after permanent recovery we measure lifetimes of $\tau_{0p}(\Delta n = 1.5 \times 10^{15}\text{cm}^{-3}) = 210\ \mu\text{s}$ without applying the RTA process and up to $\tau_{0p}(\Delta n = 1.5 \times 10^{15}\text{cm}^{-3}) = 2020\ \mu\text{s}$ using optimized RTA conditions. Apart from the very high lifetimes achieved, the applied RTA process step also strongly influences the kinetics of the permanent recovery process. The recovery process is accelerated by almost two orders of magnitude, compared to a non-treated sample, which proves the industrial relevance of the process. We discuss the results within a recently proposed defect model which ascribes the observed dependence of the kinetics of the recovery process to the presence of boron nano-precipitates and their interaction with free interstitial boron atoms.

1. Introduction

In 1974 Fischer and Pschunder [1] observed that the power output of a crystalline silicon solar cell made of oxygen-rich boron-doped silicon is significantly reduced if it is exposed to prolonged illumination. However, this reduction can be reversed if the solar cell is exposed to an elevated temperature in the absence of light. Unfortunately, this is not a stable condition and the power output decreases again as soon as the cell is illuminated. Fischer and Pschunder correlated the observed reduction of the power output to the reduction of the minority carrier lifetime in the silicon base. However, the physical origin of the lifetime reduction remained unknown.

In the following years the light-induced degradation (LID) was intensively studied and it was finally concluded that the magnitude of lifetime degradation is related to the simultaneous presence of boron and oxygen in the Czochralski-grown silicon (Cz-Si) material [2,3]. Please note that LID in silicon can also occur due to the presence of different other contaminants such as e.g. copper [4]. However, these effects can be clearly separated from the LID solely due to the presence of boron and oxygen as the lifetime degradation proceeds on very different characteristic time scales. In this contribution, we focus on the LID typically observed in boron-doped Cz-Si without any other intentional contaminations.

In 2006 Herguth et al. [5] found that the solar cell efficiency can be permanently recovered (regenerated) if the solar cell is exposed to illumination at elevated temperatures. This permanent recovery in cell efficiency was attributed to the permanent recovery of the lifetime in the base material.

As shown by Bothe et al. in a previous investigation of the influence of high-temperature treatments on the degraded lifetime, cooling ramps after a high-temperature process step shows a pronounced impact on the defect concentration and hence the level of the stable lifetime after illumination [6].

In this contribution, we resume the thought that the defect properties are affected by the cooling after the last high-temperature process step and systematically vary the cooling

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conditions of lifetime samples in a rapid thermal annealing (RTA) process, as typically applied as the metal-contact forming firing step in the industrial solar cell production. The influence of the cooling rate on the properties of the boron-oxygen related (BO) defect centers are investigated. A special focus is placed on the achievable lifetimes after the process of permanent recovery. Apart from the characteristic lifetimes, τ_d after completed light-induced degradation, τ_0 after annealing in darkness at 200 °C for 10 min, and τ_{0p} after the process of permanent recovery, the dynamics of the recovery process are also studied.

2. Sample preparation

The material used in this investigation is 150 μm thick commercially available boron-doped Cz-Si crystallized using typical growing conditions, yet unknown to the authors. The samples exhibit a resistivity of $\rho = (1.02 \pm 0.03)$ Ωcm determined via four-point-probe measurements and an interstitial oxygen concentration $[O_i] = (6.9 \pm 0.3) \times 10^{17}$ cm^{-3} determined via FTIR measurements, according to the IOC88 standard. The wafers are processed into lifetime samples at full size (156×156 mm²) using the following processing sequence: First the saw damage on the surfaces is removed by applying a KOH damage etch step (50% KOH (aqueous solution), 90 °C, 10 min). Afterwards the samples are cleaned using a standard RCA cleaning sequence. After that, a phosphorus diffusion is performed (850 °C, 1:10 h) resulting in an n^+-region with a nominal sheet resistance of 100 Ω/sq. The P-diffusion is performed in order to eliminate variations in the thermal history of the material originating from the crystal growth. After the process, the samples are removed at 800 °C from the furnace and rapidly cool down to room-temperature without temperature monitoring. Afterwards, the samples are divided into two groups until the RTA treatment is performed. One group of samples is processed into lifetime samples continuing with the removal of the phosphor silicate glass (PSG) as well as the n^+-region using HF and KOH. After another RCA cleaning sequence a 10 nm thick Al_2O_3 layer is deposited via plasma-assisted atomic layer deposition (plasma-ALD) on both sides for surface passivation. In order to improve thermal stability of the passivation layer a 70 nm thick silicon nitride capping layer (refractive index $n = 2.05$) is deposited on top of the Al_2O_3 layer via plasma enhanced chemical vapor deposition (PECVD) [7]. An additional annealing step at 425 °C for 15 min is performed to activate the passivating properties of the Al_2O_3/SiN stack [8]. The passivation of the surfaces with an Al_2O_3/SiN stack results in very low surface recombination velocities S which were previously determined by Veith et al. [9] to be lower than $S = 10$ cm/s. After processing, the samples undergo the high-temperature RTA treatment.

The second sample group contains samples that have been removed after the P-diffusion. In this group, we use the diffused region, present during the RTA, to protect the bulk material from unintended contaminations in the furnace. After the removal of the PSG, this sample group undergoes the high-temperature RTA treatment and is then processed into lifetime samples afterwards by removing the n^+-region using KOH and cleaning the surfaces in a standard RCA cleaning sequence. The sample surfaces are then passivated using 10 nm of Al_2O_3 deposited via plasma-ALD. Again, in order to establish the passivation quality of the dielectric layer, the samples are annealed on a hotplate at 425 °C for 15 min. Please note that in the second group, no SiN layer is deposited on the samples' surfaces in order to avoid possible hydrogen sources.

3. Experimental details

To systematically vary the cooling of the samples, we perform the rapid thermal annealing (RTA) step in a commercially available belt firing furnace (DO-FF-8.600–300, Centrotherm). Different cooling rates are realized by varying the peak temperature as well as the belt speed. The belt speed is varied from 1.2 m/min to 7.2 m/min. As peak temperatures we chose 650 °C and 850 °C. In order to properly correlate the lifetime results with the temperature profile the samples are exposed to, each applied temperature profile is recorded using a DATAPAQ Insight Oven Tracker with a temperature probe attached to a sample processed identically to the lifetime samples under investigation. Typical temperature profiles measured on a sample with Al_2O_3/SiN stack present during RTA are shown in Fig. 1. As can be seen, by varying belt speed and peak temperature the cooling curve after reaching the peak temperature can be varied. In general, a faster belt speed leads to a faster cooling rate of the samples from peak to room temperature. However, for specific temperature ranges this does not have to be the case. Therefore, the temperature profiles are carefully examined.

Lifetime measurements are performed using the WCT-120 lifetime tester from Sinton Instruments. If not stated otherwise the lifetimes mentioned in this contribution are all extracted at an injection-density of $\Delta n = 0.1 \times p_0$, with Δn being the excess carrier density and p_0 being the hole concentration in darkness. For the investigated material p_0 equals the boron concentration.

In this study, we analyze three characteristic lifetimes:

(a) τ_d after illumination and completed light-induced degradation (LID). The degradation is performed at room temperature and a light-intensity of 10 mW/cm² using a halogen lamp. LID is completed after 12 h of illumination.

(b) τ_0 after annealing in darkness for 10 min at 200 °C. This lifetime is used as a reference, however, it has to be kept in mind that the annealed state does not correspond to a stable defect configuration and that even low light intensities already lead to a lifetime degradation. Experimentally, this is the most difficult lifetime to be extracted.

(c) τ_{0p} after the completed process of permanent recovery, i.e. when, depending on the RTA treatment, the maximum lifetime during the recovery process is measured. The process of permanent recovery is performed using a hotplate and a halogen lamp with a light intensity of 100 mW/cm². Different recovery temperatures between 100 °C and 220 °C are chosen to investigate their influence on τ_{0p} and on the dynamics of the recovery process.

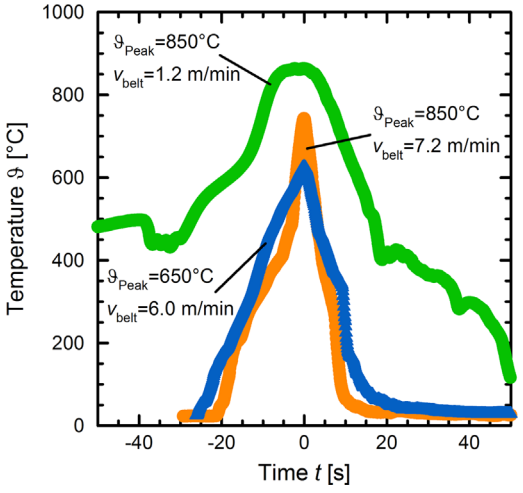

Fig. 1. Temperature profiles measured on a sample with Al_2O_3/SiN stack present during RTA, using the DATAPAQ Insight Oven Tracker. The profiles for three conditions (set-conditions) are displayed. Orange and green circles correspond to a peak temperature of $\vartheta_{Peak} = 850$ °C with belt speeds of $v_{belt} = 7.2$ m/min and $v_{belt} = 1.2$ m/min, respectively. Blue triangles to $\vartheta_{Peak} = 650$ °C and $v_{belt} = 6.0$ m/min.