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Reduction of light-induced degradation of boron-doped solar-grade Czochralski silicon by corona charging

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Abstract

This study aims at the reduction of light-induced degradation of boron-doped solar-grade Czochralski silicon wafers by corona charging. The method consists of deposition of negative charges on both surface sides of wafer and keeping the wafer in dark for 24 hours to allow the diffusion of positively-charged interstitial copper towards the surfaces. This method proves to be useful to reduce or eliminate light-induced degradation caused by copper. The degradation was significantly reduced in both intentionally (copper-contaminated) and "clean" samples. The amount of the negative charge was found to be proportional to the reduction strength

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Keywords: Light-Induced Degradation; Solar-grade; Cz-Si; Copper; Corona Charging

1. Introduction

Light-induced degradation (LID) of boron-doped Czochralski silicon (Cz-Si) wafers has been studied extensively since its discovery in 1973. It is generally believed that boron oxygen complexes are responsible for LID. Two major models for the complex have been proposed: i) B_sO_{2i} complexes formed of one substitutional boron atom B_s and two interstitial oxygen O_{2i} [1] and ii) latent complex B_iO_2 of an interstitial boron atom B_i and an oxygen dimer [2]. Avoiding oxygen or lowering the boron doping level are natural ways to reduce LID although both of these have evident drawbacks, such as increased wafer manufacturing cost or reduced cell efficiency.

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Copper has also been reported to induce LID regardless the presence of boron or oxygen [3]. It was proposed that light activation reduces the electrostatic repulsion between positively charged interstitial copper ions (Cu_i^+) and copper precipitates [4] and hence enhances copper precipitation, which decreases considerably the performance of the material.

Copper precipitates are known to be strong recombination active defects as compared to Cu_i^+ in p-type silicon [5], because they form a defect band close to the middle of the silicon bandgap [6]. Furthermore, these precipitates may be decorated with extended dislocations network due to their misfit with silicon lattice [7], leading to an enhanced recombination activity.

Recently, deposition of negative corona charges was found to reduce significantly LID in electronic-grade Cz-Si wafers intentionally contaminated by copper [8]. Negative surface charge attracts Cu_i^+ towards the surface and thus decreases the bulk concentration. Although accumulation of copper at the surface may increase the surface recombination due to a possible copper precipitation at the silicon/oxide interface, the effective minority lifetime remains rather stable under illumination. This is because there is less copper left in the bulk to react with light. .

Solar-grade silicon is widely used for solar cell fabrication due its lower cost compared to electronic-grade one, however, it contains higher level of metal impurities leading to inferior quality. Among these impurities, copper can contribute significantly to light-induced degradation. In this study, we investigate the effect of surface corona charging on LID in both clean and intentionally copper-contaminated solar-grade Cz-Si wafers.

2. Experimental

The experiments were performed on solar-grade 156×156 mm^2 boron-doped Czochralski silicon sister wafers, with the resistivity of 1-2 Ω-cm and thickness ~200µm. The wafers were cleaned by RCA1 followed by an HF dip for 2 minutes. Then, the wafers were oxidized and annealed in nitrogen at 900°C and 950°C, respectively, for 40 minutes each step. Consequently, a surface passivation was achieved with about 15 nm thermal oxide layer.

The wafers were then cut to irregular-shape samples using a diamond pen. For these experiments, three samples were taken from one wafer and kept clean without any intentional contamination. Two samples from another wafer were intentionally contaminated with copper.

The contamination was performed by spin coating 2 ppm of copper solution onto the surface of the samples. The samples were then annealed at 800°C for 20 minutes to allow copper to diffuse into the bulk. The maximum bulk copper concentration is around 1014 cm^{-3} [3] after in-diffusion anneals.

Corona charging was used to deposit positive and negative charges (+300 µC, -300 µC and -900 µC), on both surfaces of the samples and they were kept in dark for 24 hours. The positive charges would keep Cu_i^+ atoms in the bulk, whereas the negative charges attract them to the surface. Corona charging method consists of depositing ions on a surface at atmospheric pressure through potential applied to a wire, a series of wires, a single point, or multiple points located a few mm or cm above the sample surface [9]. The negative and positive corona ionic species are predominantly CO^{-3} and H_3O^+, respectively.

Next, all samples were subjected to the degradation process through illumination during 24 hours under a Xenon lamp with one sun intensity at room temperature. The initial and the final minority lifetime were measured with Microwave Photoconductance Decay (µ-PCD) by a WT-85XL Semilab lifetime scanner.

3. Results

3.1. Copper-contaminated solar-grade Cz-Si

The average lifetime of copper-contaminated samples before and after the degradation process is presented in Fig 1. The lifetime of the positively charged sample drops considerably after the degradation process. Moreover, the degraded lifetime does not recover upon annealing in dark at 200°C for 10 minutes unlike degraded lifetime observed in boron-doped clean silicon. Thereby, it seems that the degradation is mostly dominated by copper precipitation and BO-LID has only negligible effect here.

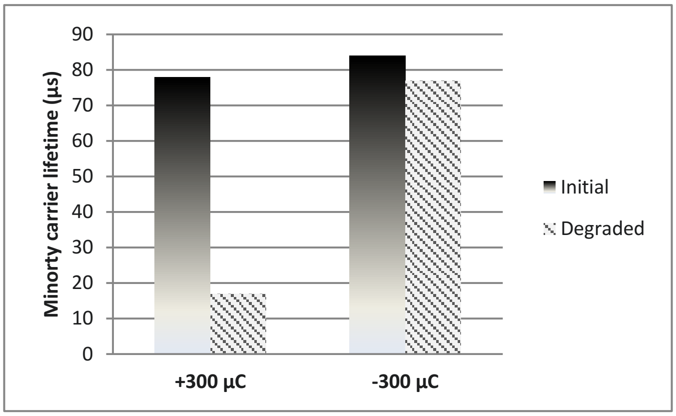

Fig.1. Average lifetime of Cz-Si samples contaminated by 2 ppm copper solution before (Initial) and after (Degraded) exposure to 24 hours of one-sun-illumination with positive and negative surface charge.

In contrast, the lifetime of the negatively charged sample hardly degrades after 24 hours of illumination. This is in agreement with the results reported in [8], where negative charge minimized significantly the light-induced degradation in electronic grade silicon wafers. Results in Fig 1 show that this method can reduce LID considerably in contaminated solar-grade silicon similarly to the electronic-grade silicon.

3.2. Clean solar-grade Cz-Si

The effect of negative charge was also tested on clean solar-grade samples. Even though this material is supposed to be clean, being solar-grade material, it contains most likely unintentional metal impurities among others copper. The average lifetime of three samples with +300 µC, -300 µC and -900 µC before and after degradation process are shown in Fig 2.

Surprisingly, the effect of the negative charge is noticeable; the degradation is reduced in the sample charged with -300 µC compared with the sample with positive charge and almost suppressed in the sample with -900 µC surface charge. The stronger effect of large negative charge was also reported in [8].

Nevertheless, the comparison is not straightforward due to the difference of the initial lifetime which drops by increasing the amount of the deposited negative charge. This effect was attributed to the fact that large amount of negative charges might deteriorate the thermal oxide surface passivation due to damage induced in $Si\text{-}SiO_2$ interface by the charge [10]. Thereby, the surface recombination velocity is higher in negatively charged samples also after degradation. Nevertheless, as the effective lifetime of the degraded samples with negative charge remains higher than that of the positively charged sample, the negative surface charge clearly reduces bulk lifetime degradation in solar-grade silicon.

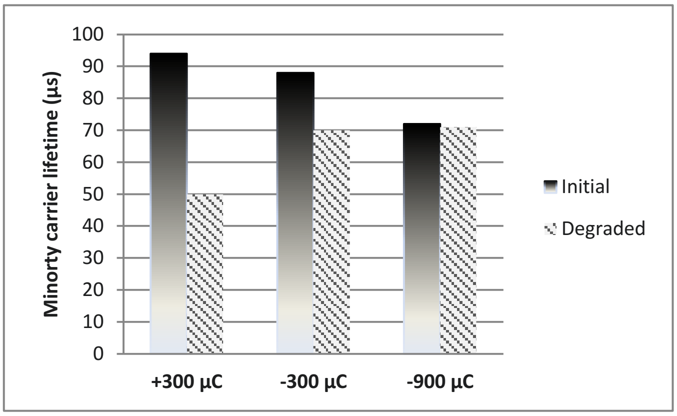

Fig.2. Average lifetime of "clean" Cz-Si samples before (Initial) and after (Degraded) exposure to 24 hours of one-sun-illumination with positive charge and two levels of negative surface charge.

The stronger effect of negative charge on the reduction of LID on the Cu-contaminated sample compared to the clean ones is likely due to the lower concentration of Cu in the second case.

It was reported in [8] that negative charge has only a marginal effect on the clean electronic-grade silicon, which means that the positive impact of negative charge on LID applies only on silicon containing a certain level of interstitial copper. Apparently, both Cu-LID and BO-LID are deactivated by negative charge when Cu-LID dominates. The mechanism behind this deactivation is unclear since the interaction nature between BO complexes and Cu precipitates remains, so far, unknown. Yet, it is confirmed [3] that boron and oxygen (especially oxygen precipitates) interact with copper and enhance Cu-LID. More investigations are needed to identify and clarify Cu-BO interactions.

It was suggested in [3] that Cu concentrations as low as 10^9 cm^{-3} can induce degradation. This is below the detection limit of most of the available chemical analysis techniques; therefore, Cu-induced degradation can occur even in material where Cu is not detectable.

In summary, our results presented here indicate that Cu plays an important role in the light-induced degradation of solar-grade material, since negative charge on the surface had a clear impact on the degradation. Thus, copper cannot be ignored as a source of LID in solar-grade Cz silicon, and the optimization of the surface charges could provide a powerful tool to reduce/eliminate the light-induced degradation.

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