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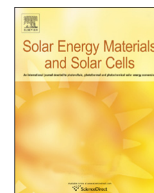

Hydrogen induced degradation: A possible mechanism for light- and elevated temperature- induced degradation in n-type silicon

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ABSTRACT

In this work, we demonstrate a form of minority carrier degradation on n-type Cz silicon that affects both the bulk and surface related lifetimes. We identify three key behaviors of the degradation mechanism; 1) a firing dependence for the extent of degradation, 2) the appearance of bulk degradation when wafers are fired in the presence of a diffused emitter and 3) a firing related apparent surface degradation when wafers are fired in the absence of an emitter. We further report a defect capture cross-section ratio of $\sigma_n/\sigma_p = 0.028 \pm 0.003$ for the defect in n-type. Utilizing our understanding of light and elevated temperature induced degradation (LeTID) in p-type silicon, we demonstrate that the degradation behaviors in both n-type and p-type silicon are closely correlated. In light of numerous reports on the involvement of hydrogen, the potential role of a hydrogen-induced degradation mechanism is discussed in both p- and n-type silicon, particularly in relation to the diffusion of hydrogen and influence of hydrogen-dopant interactions.

1. Introduction

Light- and elevated temperature- induced degradation (LeTID) has generated significant interest in both academic and industrial circles of the photovoltaics industry. Initially, this phenomenon was observed to negatively impact the lifetime and electronic characteristics of devices and wafers fabricated on p-type multi-crystalline silicon wafers, especially on those utilizing the higher efficiency passivated emitter and rear contact (PERC) cell technology [1]. Numerous studies have undertaken detailed defect analysis studies and defect formation and recovery kinetics in an effort to identify a possible root cause [2–6]. A key behavior identified by Chan et al. and Bredemeier et al. is the modulation of the extent of LeTID with firing temperature, with an increasing extent of degradation with increasing firing temperature, and the absence of degradation in unfired samples [2,3]. Many recent studies have also postulated the involvement of hydrogen in the formation of and as a possible root cause for LeTID, although the true nature of the involvement of hydrogen is far from understood [7–11]. Kersten et al. demonstrated that LeTID was only observed on samples that had been fired in the presence of a hydrogen containing dielectric layer such as passivating hydrogenated silicon nitride (SiN_x:H) and aluminium oxide (AlO_x:H) films [12]. Vargas et al. demonstrated a manipulation of the LeTID related degradation by varying the hydrogen fraction in SiN_x:H films, thus showing a correlation between degradation extent and the amount of hydrogen released from the dielectric [13]. Hydrogen as a component of the LeTID defect would be in agreement with the strong firing dependence of LeTID; where a greater in-diffusion of hydrogen from the dielectric layers may occur at higher temperatures [9,14].

Of particular interest for this work are the recent observations of Bredemeier et al. [5]. Their results provided evidence that the recovery in lifetime after degradation was driven by the diffusion of some species to the wafer surface. They highlighted that nickel or cobalt could possibly be the fast diffusing defect, although they could not rule out the involvement of hydrogen. However, it was suggested that, instead, the in-diffusion of hydrogen from the surface would result in the passivation of the defect.

Recent studies by Chen et al. and Fertig et al. have shown that the identical defect can also manifest itself within solar cells fabricated on p-type Czochralski-grown silicon [15,16]. Since then, similar observations of degradation on float-zoned (FZ) silicon have been proposed to arise from identical defects [11,17,18]. In these FZ-LID studies, Sperber et al. observed an initial bulk deterioration followed by subsequent declines in surface passivation quality [18].

N-type silicon has been long lauded for its low susceptibility to both

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light-induced degradation such as the boron-oxygen related degradation and the detrimental impacts of metallic contaminants [19]. Although this material does indeed suffer from degradation induced by grown-in defects, which have been extensively studied [20], an investigation of LeTID on n-type silicon by Niewelt et al. concluded that the defect either does not manifest itself or is not recombination active in n-type [11]. On the other hand, a study by Renevier et al. demonstrated a carrier-induced instability in the lifetime of boron-diffused n-type wafers fired in the presence of a hydrogen-rich dielectric when subject to either illuminated annealing or dark annealing [21]. Although it was determined that phosphorus diffusions resulted in a suppression of the degradation phenomenon, and that degradation did not occur in the presence of a silicon-rich (low-hydrogen content) silicon nitride layer or an aluminium oxide layer, a lack of understanding of the defect and of LeTID at the time resulted in unclear conclusions.

In this paper, we further extend the work of Renevier et al. [21]. With increased understanding of LeTID and its behavior under various testing conditions, we demonstrate that n-type silicon can be susceptible to LeTID, with behaviors akin to the defect observed in studies on p-type silicon. We investigate the importance of a diffused emitter both during firing and LeTID testing and correlate observed behaviors with various models described in literature. In light of recent work suggesting the involvement of hydrogen as a cause of LeTID, we present an explanation of our experimental results using a model of hydrogen reactions and diffusions and hypothesize a likely hydrogen induced degradation mechanism.

2. Methodology

2.1. Sample preparation

To carry out our investigations of LeTID, symmetrical lifetime precursors were fabricated on commercially acquired silicon wafers. For n-type specimens, we used neighboring 156 mm × 156 mm uncompensated n-type phosphorus-doped 2 Ω cm Czochralski-grown wafers with a thickness of 190 ± 2 µm obtained from Woongjin Energy. These as-cut wafers were placed in potassium hydroxide solution to remove saw damage and subsequently textured to a final thickness of 183 ± 3 µm in an alkaline texturing bath. The wafers were then cleaned using the radio corporation of America (RCA) 1 and 2 processes, that is; a 6 min dip in ammonium hydroxide (NH_3OH) and hydrogen peroxide (H_2O_2) solution and a subsequent 6 min clean in a solution of hydrochloric acid (HCl) and hydrogen peroxide. This is then followed by a short HF dip to remove any oxides that may be present. The wafers were then split into 3 groups. Wafers in Group 1 received a boron diffusion in a boron tribromide (BBr_3) -diffusion furnace at temperatures of ≈ 920 °C resulting in a p^+-emitter with a sheet resistance of R_{sheet} = (95 ± 5) Ω/sq. Using these conditions, we avoid generating SRH recombination centers from misfit dislocations described by Cousins and Cotter [22]. Afterwards, dilute hydrofluoric acid (DHF) (2% v/v) was used to remove borosilicate glass from the surface. Group 2 wafers were also diffused in a phosphoryl chloride ($POCl_3$) diffusion furnace to apply a phosphorus diffused n^+-emitter with sheet resistance of R_{sheet} = (60 ± 3) Ω/sq. Similarly, DHF was used to remove any phosphosilicate glass from the surface. Group 3 wafers did not receive any diffusion process. All wafers were then RCA cleaned again before deposition of dielectric layers. A 75 nm layer of hydrogenated silicon nitride (SiN_X:H) film with a refractive index of 2.08 at 633 nm [23] was deposited on both sides using a Meyer Burger MAiA remote plasma enhanced chemical vapor deposition (r-PECVD) tool [24]. Once deposited, wafers were fired in an in-line Schmid metallization fast-firing belt furnace at a range of setpoint temperatures between 700 °C and 900 °C (actual sample temperatures between 598 °C and 815 °C) and a set conveyer speed of 4.5 m/min. Actual temperatures were measured on identical dummy wafers using a Q13 Datapaq temperature profiler averaged using three K-type thermocouples

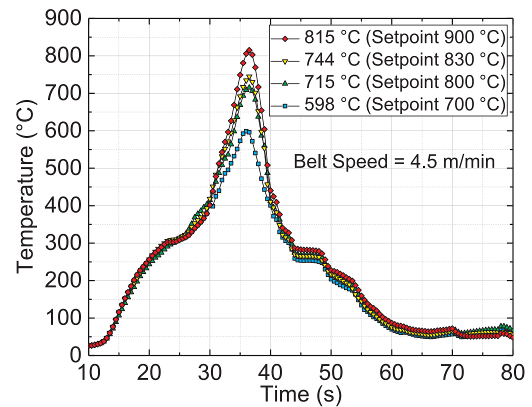

Fig. 1. Belt-furnace firing profiles measured on wafers undergoing various firing recipes ranging with actual temperatures of 598 °C (cyan squares), 715 °C (green upward triangles), 744 °C (yellow downward triangles) and 815 °C (red diamonds). Setpoint temperatures are shown in parentheses within the legend. Lines are shown to serve as a guide to the eye. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

(Omega KMQXL-IM075G-300). Due to the importance of the firing condition for defect formation, the measured profiles are shown in Fig. 1 below. Additional unfired wafers were kept as controls. The six-inch wafers were then laser cleaved into 52 mm × 52 mm tokens. The central token from each substrate was taken for experimental use due to variations in sheet resistivity from diffusion non-uniformities around the edge of the 6-in. wafer. As a comparison to n-type, a set of p-type high-performance multi-crystalline wafer acquired from GCL Energy Holdings in the same group to those used in [16] were processed in parallel. These wafers were 156 mm × 156 mm boron-doped wafers with a base resistivity of 1.6 ± 0.1 Ω cm and thickness of 192 ± 4 µm. Adjacent 'sister' wafers were chosen from the ingot to ensure similar crystallographic and electrical properties. After texturing in acidic solution, these multi-crystalline silicon wafers were processed in an identical fashion to those in Group 2 described above.

2.2. Testing for LeTID

Initial testing for LeTID behavior was carried out using a dark annealing process proposed by Chan et al. and Chen et al. [9,16]. Wafers were placed on a hotplate in the dark and annealed at a temperature of 175 ± 5 °C. In parallel, a conventional light soaking process at elevated temperature was used to test for LeTID under illumination. Samples were exposed to light with an illumination intensity of 0.96 kW/m^2 (S305C, Thorlabs) supplied using four broadband halogen lamps whilst on a hotplate heated to approximately 75 ± 2 °C. Ex-situ quasi-steady-state photoconductance (QSSPC) measurements were carried out periodically during LeTID testing using a photoconductance tool (Sinton Instruments, WCT-120TS) [25]. Measurements of minority carrier lifetime were analyzed using the generalised method proposed by [26] and references therein and intrinsic recombination was corrected using the model developed by Richter et al. [27]. Effective minority carrier lifetimes (τ_{eff}) were extracted at an injection level (Δn) equal to approximately 0.1 times the background dopant density N_d (i.e. $\Delta n = 2.4 \times 10^{14}$ cm^{-3} for n-type and $\Delta n = 9.1 \times 10^{14}$ cm^{-3} for p-type samples). The apparent normalised defect density (NDD_{app}) metric was used to evaluate the evolutions in effective carrier lifetime between samples [28]:

$$NDD_{app}(\Delta n) = \frac{1}{\tau_{eff}(\Delta n)} - \frac{1}{\tau_{fired}(\Delta n)}$$

Due to the nature of the investigation on samples with various processing conditions, NDD_{app} is used to provide a qualitative

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