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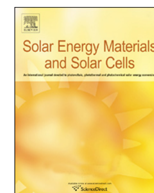

On improved passivation stability on highly-doped crystalline silicon and the long-term stability of regenerated Cz-Si

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ABSTRACT

Different surface passivation approaches are applied on Cz-Si and FZ-Si samples and long-term stability is investigated during treatments at 60–80 °C and up to 1 sun equivalent illumination intensity. It is shown that SiN_x:H and AlO_x:H/SiN_x:H surface passivation show a much more stable passivation quality when deposited on P-diffused and B-diffused surfaces, respectively. Long-term measurements lead to the conclusion that Cz-Si samples fired at measured peak temperatures up to 750 °C are very stable after regeneration of bulk defects. Samples fired at 850 °C show much stronger bulk-related degradation potentially linked to light and elevated temperature induced degradation (LeTID). Furthermore, Cz-Si samples fired at 850 °C express an instable behavior after a regeneration treatment.

1. Introduction

A high bulk minority carrier lifetime τ_b is required in solar cells to enable high conversion efficiencies. It is well known that light induced degradation (LID) during operation of solar cells may degrade τ_b significantly, *e.g.*, due to the formation of boron-oxygen (BO) related defect centers [1–4] or copper related LID [4]. A few years ago, it was discovered that another type of LID, frequently called light and elevated temperature induced degradation (LeTID), may significantly decrease τ_b, too [5–7]. Both BO-LID and LeTID can be regenerated during or after sample preparation, allowing for high and supposedly stable τ_b [8–11]. However, the amount of studies on the long-term stability of regenerated Czochralski silicon (Cz-Si) samples is rather sparse. In [12–14], slight instabilities have been observed during stability tests of Cz-Si samples after a regeneration treatment and it has been suspected that the formation of defects not related to BO-LID are the main cause of these instabilities.

Usually, it is not τ_b but the effective minority carrier lifetime τ_{eff} which is measured in LID experiments and influenced by recombination in the bulk and at the surface of a sample. Accordingly, surface related degradation (SRD) as observed in [15–17] can pose a significant challenge for light induced degradation studies aiming at changes in the silicon bulk [16]. Especially in long-term stability studies, even slight changes in surface passivation quality can easily be misinterpreted as changes apparently occurring in the bulk. Fig. 1(a) shows a long-term stability measurement conducted after a regeneration treatment of a lifetime sample made from non-diffused B-doped Cz-Si passivated with SiN_x:H. As can be seen, τ_{eff} decreases significantly after several thousand hours of treatment at 60 °C and 0.1 suns. This long-term decrease could easily be interpreted as an instability of the regenerated state of the BO related defect. However, the simultaneous rise of the surface related saturation current density J_0 indicates that this degradation is surface related.

Passivation with AlO_x:H/SiN_x:H stacks results in more stable passivation quality compared to single SiN_x:H layers on non-diffused silicon [16]. After prolonged treatment at 80 °C and 1 sun, however, even an AlO_x:H/SiN_x:H passivated sample is slightly affected by SRD as can be seen by rising values of J_0 in Fig. 1(b) (note the different scale). Accordingly, both passivation approaches are not ideally suited for the investigation of long-term stability of τ_b.

Significant degradation of SiN_x:H based passivation already at 60 °C and 0.1 suns additionally raises the question if solar cells could suffer from SRD, too. However, SiN_x:H is usually not applied on B-doped silicon but on highly P-doped emitter layers. At treatment temperatures of 150 °C, we have recently observed a significant reduction of SRD on float-zone silicon (FZ-Si) samples with diffused surfaces ([17], to be published). Accordingly, heavily doped surfaces could be useful both for an enhanced stability of solar cells and for long-term LID studies on lifetime samples.

In this contribution, the stability of passivation quality of dielectrically passivated diffused surfaces will be examined at lower temperatures typical for solar cell operation or long-term stability studies. Advantages and disadvantages of using diffused layers in LID experiments will be discussed and the application of different passivation

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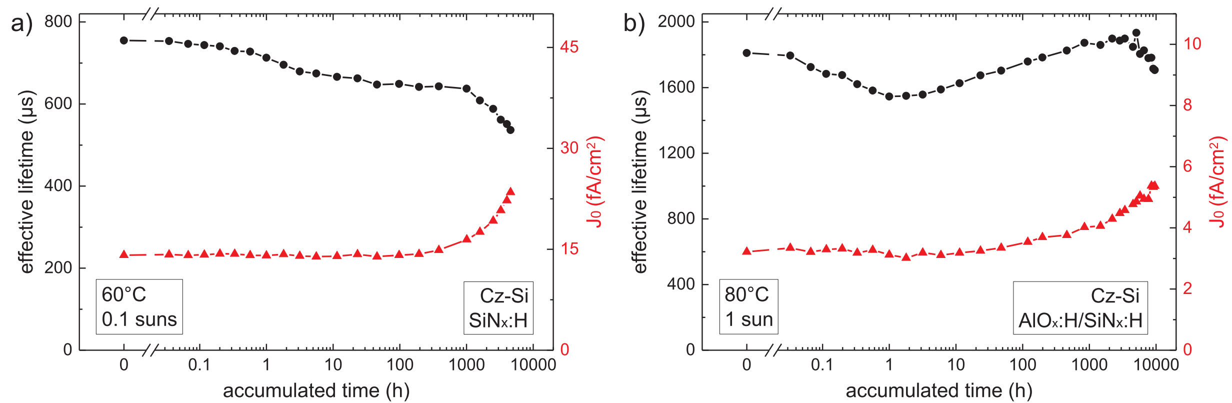

Fig. 1. Measurement of τ_{eff} and J_0 of B-doped Cz-Si samples (doping density $N_d \approx 7{\cdot}10^{15}$ cm^{-3}) passivated with (a) SiN_x:H and (b) AlO_x:H/SiN_x:H. Both samples were fired at ~750 °C and received a treatment at 150 °C and 1 sun for 12 min to regenerate bulk defects. Samples were then tested for long-term stability at 60 °C and 0.1 suns or 80 °C and 1 sun as shown in the graphs.

schemes gives new insight into the long-term stability of regenerated Cz-Si samples fired at different temperatures.

2. Material and methods

If not stated otherwise, samples were made of B-doped FZ-Si or Cz-Si wafers with doping density $N_d \approx 7{\cdot}10^{15}$ cm^{-3}. The wafers were etched in KOH to a thickness d ≈ 180 µm and received a chemical polish (CP) in a solution of acetic acid, HNO_3 and HF. To clean wafer surfaces, the wafers were oxidized in a solution of H_2O_2 and H_2SO_4 at 80 °C and the resulting surface oxide was removed in diluted HF (Piranha clean). Wafers were then processed as shown in Fig. 2. Diffusion in $POCl_3$ ambient was carried out at 840 °C and resulted in heavily P-doped n^+ layers with sheet resistance ~55 Ω/sq. The resulting phosphosilicate glass at the sample surface was removed in diluted HF and the emitter was etched back to ~120 Ω/sq. in an aqueous solution of HF, HNO_3 and $NaNO_2$ to reduce the impact of the heavily P-doped surface layer (kink region) on recombination [18]. Other samples received a BBr_3 diffusion at a drive-in temperature of 910 °C followed by etching in diluted HF to remove the boron silicate glass at the sample surface. This resulted in p^+ doped layers with sheet resistance ~100 Ω/sq. Diffused samples received another Piranha clean. Other wafers received no diffusion to serve as reference samples.

P-diffused wafers and references were coated with ~75 nm SiN_x:H using a direct plasma enhanced chemical vapor deposition (PECVD) at 450 °C and 40 kHz. B-diffused wafers and references received a passivation stack consisting of 10 nm AlO_x:H grown by atomic layer deposition (ALD) at 300 °C capped with ~75 nm SiN_x:H in a remote PECVD at 400 °C and 2.45 GHz. SiN_x:H layers had a refractive index n ~2.0 at 600 nm. All diffusions and coatings were applied to both wafer sides, resulting in symmetrical samples. After laser-cutting to an edge length of 5 cm, samples were fired in a fast firing belt furnace at a belt speed of 6000 mm/min. Peak temperatures during firing were measured at the sample surface using a sheathed type K thermocouple of diameter 0.25 mm (Omega HKMQIN-IM025U-500). Due to varying hydrogen content in the different layers and differences in SiN_x:H deposition temperatures, the degree of bulk and surface hydrogenation of SiN_x:H and AlO_x:H/SiN_x:H passivated samples may vary significantly after firing. After processing, samples were stored in darkness until measurement series were carried out.

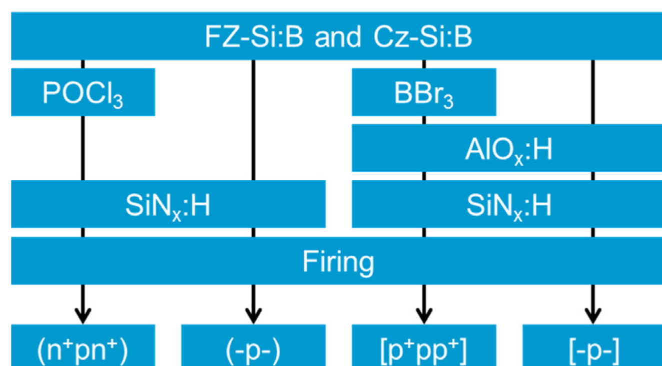

Fig. 2. Process flow and labeling of samples. Sample names indicate the sample structure and different brackets relate to different dielectric passivation layers.

In measurement series samples were treated on hotplates at constant temperature and halogen lamp illumination as indicated in each measurement. The illumination intensity is given in sun equivalents ("suns") where one sun equivalent illumination was achieved by matching the short circuit current of a solar cell to that under a solar spectrum simulator [19]. During treatment, τ_{eff} was repeatedly measured using the generalized mode [20] of a Sinton Instruments lifetime tester (WCT-120) [21] at 30 °C. If not stated otherwise, τ_{eff} is shown at an excess minority carrier density $\Delta n = 0.1{\cdot}N_d$.

The surface related saturation current density J_0 was extracted from lifetime data according to the method described in [22]. For samples with diffusion J_0 equals the emitter saturation current density J_{0e}, while for non-diffused samples J_0 equals the surface saturation current density J_{0s} [23].

Selected samples had their passivation layer removed after a measurement series by etching in 10% HF. In a next step, ~4 µm were removed on each sample side using a CP etch before samples received two Piranha cleans. Afterwards, samples were wet-chemically passivated using an 0.08 M iodine ethanol solution [24,25] and τ_{eff} was measured immediately thereafter.

3. Results and discussion

3.1. Stability of SiN_x:H passivated samples

Fig. 3 shows measurement series conducted on SiN_x:H passivated samples with (full symbols) and without (empty symbols) P-diffused surface fired at ~750 °C measured sample temperature. All samples were treated at 80 °C and 1 sun illumination. While the Cz-Si samples (red) show a pronounced bulk related minimum I and maximum II in the first hours of treatment as expected due to BO degradation and regeneration, the FZ-Si samples (black) show only minor instabilities during the first hours. After prolonged treatment, samples without emitter (-p-) show significant SRD leading to a pronounced decrease of τ_{eff} correlated with a significant rise of J_0 in good agreement with results discussed in [15,16].

We have observed before that P-diffused (n^+pn^+) samples made of

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