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Influence of defect type on hydrogen passivation efficacy in multicrystalline silicon solar cells

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ABSTRACT

We examine the effectiveness of hydrogen passivation as a function of defect type and microstructure at grain boundaries (GBs) in multicrystalline silicon. We analyze a solar cell with alternating mm-wide bare and SiN_x-coated stripes using laser-beam-induced current, electron backscatter diffraction, X-ray fluorescence microscopy, and defect etching to correlate pre- and post-hydrogenation recombination activity with GB character, density of iron-silicide nanoprecipitates, and dislocations. A strong correlation was found between GB recombination activity and the nature/density of etch pits along the boundaries, while iron silicide precipitates above detection limits were found to play a less significant role. Copyright © 2010 John Wiley & Sons, Ltd.

KEYWORDS

hydrogen passivation; defects; dislocations; iron; multicrystalline silicon

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In crystalline silicon solar cells, the introduction of hydrogen is well known to passivate defects and improve the conversion efficiency [1–3]. It has been found that the effectiveness of hydrogen passivation of grain boundaries (GBs) depends on GB character and metal contamination [4–8]. However, a deeper microstructural understanding concerning which defects are most effectively passivated, and which respond poorly to hydrogenation, is needed to guide the optimization of solar cell manufacturing. Those defects with the weakest response to hydrogenation can be most effectively dealt with during other steps in solar cell manufacturing such as crystallization or optimized emitter diffusion.

To investigate the passivation ability of hydrogen on defects at GBs in silicon, a 12.5 × 12.5 mm² multicrystalline silicon (mc-Si) solar cell was produced by IMEC. The sample contains both control (bare) and experimental (SiN_x-coated) regions, to ensure identical thermal profiles for the control and experimental regions during crystal growth and cell processing. After emitter diffusion (845°C, 12 min POCl₃ followed by 18 min drive-in) the sample was selectively masked with a ceramic paste via screen-printing

to create alternating mm-wide stripes of bare and coated regions during the deposition of the SiN_x antireflection coating and resulting hydrogenation (PECVD, 400°C, 6 min). The ceramic paste was removed after SiN_x deposition using an H₂SO₄:H₂O₂ cleaning solution. Finally, silver- and aluminum-based metal contacts were screen-printed on the front and back, respectively, and fired (RTA, T_{max} = 800°C, 4 min) in a conventional belt furnace. The electrical performance of the solar cell was characterized using laser-beam-induced current (SR-LBIC) [9] at the University of Konstanz at 833 and 910 nm. An 833 nm LBIC map is shown in Figure 1(a) illustrating regions of high (light gray) and low (dark gray) minority carrier diffusion length. It is evident from Figure 1(a) that there is a wide range of responses of GBs to hydrogen introduced during the annealing of the SiN_x coating (firing). Some GBs showing strong recombination activity in bare regions are nearly completely passivated (i.e., contrast between GB and surrounding grain is close to zero). Other GBs show almost no response to hydrogen, exhibiting similarly high LBIC contrasts in both bare and SiN_x-coated regions.

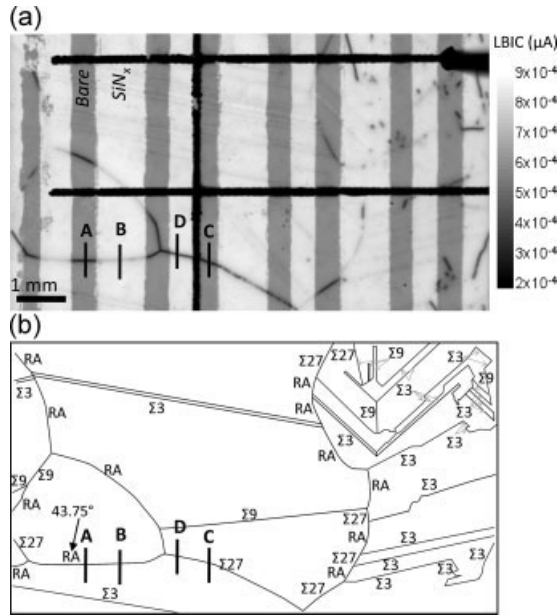


Figure 1. LBIC and EBSD of sample. (a) LBIC measurements (833 nm wavelength, 10 μm step size) were used to identify grain boundaries of high and low recombination activity. Dark gray stripes correspond to bare regions, while lighter gray stripes are SiN_x-coated. Black lines correspond to metallization. (b) Grain boundary types were identified by electron backscatter diffraction. Labels A to D correspond to the regions of interest. Grain boundaries labeled RA refer to CSL higher than 181 but well-known misorientation angles as shown in regions A and B.

The same area was also mapped using electron backscatter diffraction (EBSD) to determine the crystallographic orientations of the GBs under study. Previous works have shown a strong interdependence between GB recombination activity, GB type [10,11], and the density of metal silicide precipitates [12]. When possible, the GB was classified by its coincidence site lattice (CSL) index (Σ value); otherwise when the Σ value exceeds 181, the GB is denoted as “random angle” (RA). This notation does not imply the angles cannot be determined; on the contrary, it usually corresponds to well-established high-angle misorientations.

Guided by the LBIC map of Figure 1, four regions (labeled A, B, C, D in Figure 1) were selected for closer analysis. The regions were selected from two different types of GBs: an RA GB, which corresponds to a misorientation of 43.8° that passivated due to hydrogenation, and a Σ 27a GB, 31.2° misorientation that did not exhibit an electrical improvement after passivation. From each GB, one bare region and one SiN_x-coated region were selected. High-resolution LBIC linescans at 833 and 910 nm were taken; these are shown in Figure 2, where the sub-figures (a–d) correspond to the labels (A–D) in Figure 1.

The high-resolution LBIC linescans (Figure 2) were fit to a model [13], which considers the GB as a two-dimensional interface between neighboring grains of uniform diffusion length; the model outputs the effective surface recombination velocity (SRV) of the GB. As reported by Micard *et al.* [13], the fitting procedure uses the LBIC value of the plateau level away from the boundary. The SRVs are then obtained by fitting the profiles normalized by the plateau levels to a theoretical

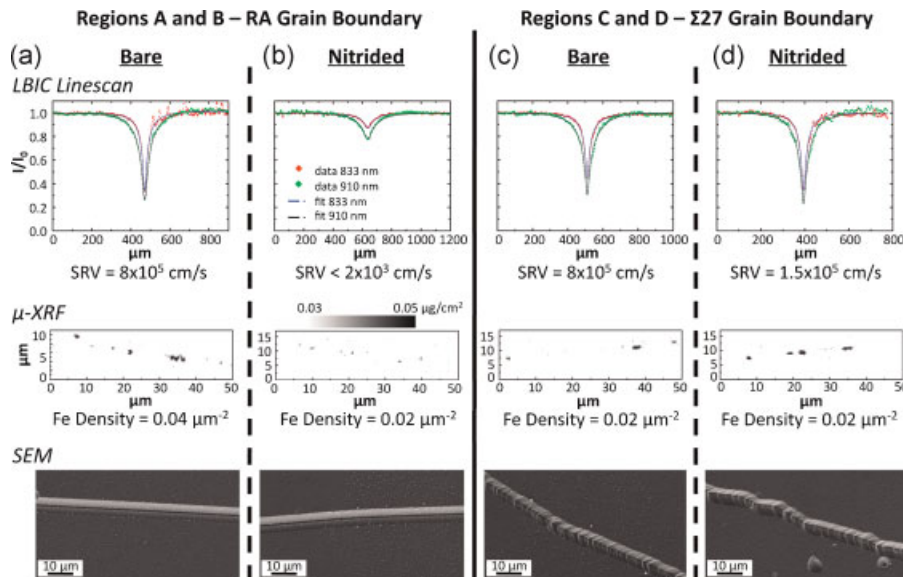


Figure 2. Comparison of passivating and non-passivating grain boundaries. Four regions of the sample (a), (b), (c) and (d) corresponding to points A, B, C, and D from Figure 1 were studied by high-resolution LBIC, μ-XRF, and SEM. μ-XRF data shows Fe-rich particles, given in a real density (particles/μm²) along the GB, accurate to within an order of magnitude based on the calculated exit angle of the grain boundary. SEM images show a significant difference in the order and spacing of dislocation etch pits along the two different boundaries. This figure is available in color online at www.interscience.wiley.com/journal/ptp

expression. The calculated SRVs are only slightly dependent on injection level; the uncertainties due to differences in injection levels between the nitride-coated and bare regions is estimated to be less than 20%.

The SRV in both the RA and $\Sigma 27$ GBs was 8×10^5 cm/s in the bare regions. In the SiN_x -coated regions, this RA GB was observed to have a marked decrease in LBIC contrast, corresponding to a reduction of the SRV to below 2×10^3 cm/s. Conversely, this $\Sigma 27$ GB showed a mild reduction in LBIC contrast, corresponding to an SRV of 1.5×10^5 cm/s.

Of interest is the fact that the LBIC linescan profile of the nitrated boundary in Figure 2(d) has a larger contrast than the bare boundary in Figure 2(c), even though the estimated SRV is lower. This apparent discrepancy can be explained by differences in bulk minority carrier diffusion length. The bulk minority carrier diffusion length in the nitride-coated region ($L_{\text{diff}} = 200\text{--}300 \mu\text{m}$) is larger than in the bare regions ($L_{\text{diff}} = 130 \mu\text{m}$), thus a smaller SRV in SiN_x -coated region can produce a larger LBIC contrast.

Synchrotron-based X-ray fluorescence microscopy (μ -XRF, Figure 2) was used to detect metal silicide nanoprecipitates at these GBs. At Beamline 2-ID-D [14] at the Advanced Photon Source of Argonne National Laboratory, a beam of 10 keV X-rays focused to a 200 nm beam-spot size was used to map the four regions of interest. These maps revealed the presence of Fe-rich particles between 50 nm and $2 \mu\text{m}$ in diameter decorating the GBs. It should be noted that an incoming X-ray energy of 10 keV permits the detection by μ -XRF of the most common and detrimental metallic species in silicon (i.e., Cu, Ni, Fe, Cr); however, only iron was found during these scans. The angle of the GB relative to the sample surface was estimated from the elastically scattered X-ray signal, and the approximate density of the precipitates decorating the grain was calculated. These μ -XRF results confirm the presence of Fe in the sample, which is known to be a major source of recombination activity in mc-Si solar cells [15]. Previous reports have shown that the composition of these particles along GBs is mostly FeSi_2 [16]. Despite the fact that GB SRV was found to vary over two orders of magnitude (Figure 2), the density of Fe particles was found to be similar along these two GBs investigated, suggesting that the post-passivation recombination activity of the GB shown in Figure 2(d) cannot be singularly attributed to the presence of the detected Fe-rich nanoprecipitates at these spatial densities.

Finally, to reveal dislocations present along the GBs, the sample was defect etched. After removal of the metallization and SiN_x layer by etching in HF, one side of the sample was polished, and then cleaned in a 9:1 by volume solution of nitric:hydrofluoric acids for 30 s. Next, the sample was etched in a Sopori mix [17] while agitated for 30 s and finally rinsed in deionized water and air-dried. This process revealed $\sim 5 \mu\text{m}$ etch pits where dislocations exit the surface of the sample.

Scanning electron microscope (SEM) images of the four regions of interest along the RA and $\Sigma 27$ GBs are shown in

Figure 2. The absence of individual observable etch pits along the RA GB indicates a high degree of order; the dislocation cores of the misfit dislocations present along the boundary are so close together that etch pit counting is not possible. This is consistent with literature reports of misfit dislocation spacing on the order of a couple to tens of nanometers, depending on the angle of misorientation between adjacent grains [18].

On the other hand, the $\Sigma 27$ GB appears jagged (faceted) with a quantifiable number of etch pits. The spacing between the etch pits in this $\Sigma 27$ boundary varies from 0.5 to $2 \mu\text{m}$, which is two orders of magnitude higher than the typical distance between regularly spaced misfit dislocations [19]. These dislocations are positioned at the corners of step-like features with a consistent angle of 160° . The origin of these etch pits is most likely related to the GB faceting, as described by Andreeva *et al.* [19], where $\Sigma 27$ boundaries were found to be structurally unstable with a tendency to facet along the $\{111\}$ planes of the adjacent grains. Higher-order twin boundaries ($\Sigma 3^n$) are known to facet, often after heat treatments [20]. The facets are usually well defined with respect to the CSL GB and are normally parallel to close-packed planes of the CSL GB. TEM investigations have demonstrated the instability of $\Sigma 27$ boundaries in silicon, which tend to dissociate into a series of 100 nm triangular grains, consisting of a coherent $\Sigma 3$, a $\{122\}$ $\Sigma 9$, and a $\{111\}/\{115\}$ $\Sigma 9$ boundary, which is consistent with the 160° angle we report [21]. Note that faceting has also been reported to increase $\Sigma 27$ GB recombination activity; electron-beam-induced current measurements have shown that the SRV for the symmetric orientation of the $\Sigma 27$ GB is an order of magnitude smaller than the corresponding asymmetric (faceted) orientations of the GB [19–22].

Figure 3 compares the LBIC contrast before and after passivation for all the GBs that were long enough to have a region in the bare and SiN_x -coated stripes. LBIC contrast of a given GBs is defined by

$$C = \frac{I_{\text{grain}} - I_{\text{GB}}}{I_{\text{grain}}}, \quad (1)$$

where LBIC intensity (I) was measured at the GB and within the grain (data shown in Figure 1(a)), providing a quantitative measure of the recombination activity of the GB.

Figure 3 illustrates the effectiveness of hydrogen passivation as a function of GB character. The recombination activity (LBIC contrast) of the same GBs is evaluated with and without a passivating SiN_x coating. Data points falling well below the 1:1 line represent GBs that passivated well.

From Figure 3, two classes of GBs can be distinguished, typified by GBs (A,B) and (C,D). GBs with LBIC contrast that reduces significantly after passivation exhibit negligible faceting, and no discernable dislocation etch pits. Meanwhile, GBs with unchanged or even higher LBIC contrast after passivation possess a disordered/faceted characteristic (see SEM images in Figure 3). For these

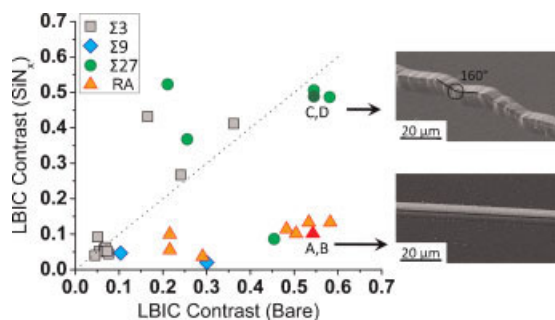


Figure 3. LBIC contrast of long grain boundaries. LBIC contrast before and after passivation is compared for individual GBs. The dotted diagonal line represents zero passivation improvement. Data points falling well below this line correspond to grain boundaries that are effectively passivated. Conversely, GBs falling nearby this line do not passivate. Scanning electron micrographs of typical passivating and non-passivating grain boundaries are illustrated to the right; labels A, B, C, and D refer to regions designated in Figures 1 and 2. Note the 160° faceting angle characteristic of non-passivating GBs. This figure is available in color online at www.interscience.wiley.com/journal/PIP

GBs, we compare LBIC contrast versus the density of visible etch pits per unit length along the GB (Figure 4). The correlations between etch pit density and LBIC contrast before and after hydrogenation (Figure 4) present a clear trend of higher passivation efficacy with lower dislocation etch pit density. This observation is in line with work by Donolato, who related electron beam induced current (EBIC) to the density of dislocations in a boundary plane [23].

The dependence of LBIC contrast on etch pit density (Figure 4) suggests that dislocations, possibly related to faceting, along the GB are the primary defect limiting improvement of GB recombination activity after hydrogen passivation. Due to the presence of large Fe-silicide precipitates detected along the GBs (Figure 2), one could also expect impurity point defects or smaller precipitates (below our μ -XRF detection limit) to decorate the dislocations, contributing to their recombination activity. This would be consistent with previous work suggesting that the interaction between Fe and GB structure governs the recombination activity of certain GBs [12,24–26]. Our observations are also consistent with a recent report by Sarau *et al.* [27], which indicates that the stress associated with this type of GB faceting is correlated to GB electrical activity.

In conclusion, LBIC studies on a specially prepared mc-Si solar cell sample containing mm-wide stripes of bare and SiN_x -coated regions indicate that the recombination activity at some GBs reduces significantly upon hydrogen passivation, whereas other GBs do not, consistent with literature reports. Our detailed analytical investigations demonstrate that defect microstructure plays a dominant role in determining passivation efficacy. μ -XRF, EBSD, and defect etching reveal that the density of countable etch pits, likely related to the high degree of faceting of the GB,

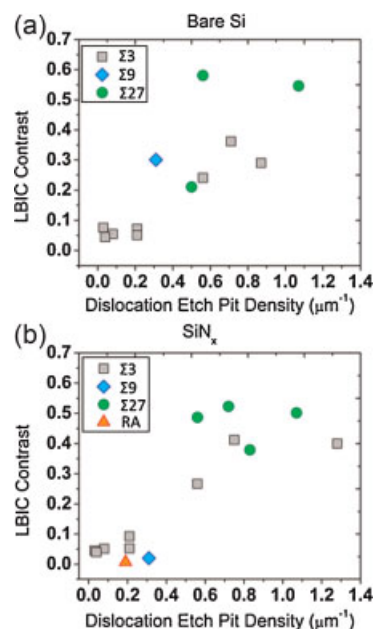


Figure 4. Recombination activity of grain boundaries by type and dislocation density for (a) bare silicon and (b) hydrogen passivated regions. LBIC contrast is plotted versus dislocation etch pit density (EPD) for GBs exhibiting little to no improvement after hydrogenation (upper points in Figure 3). Note a strong proportional dependence of GB recombination activity on EPD both before and after hydrogenation. This figure is available in color online at www.interscience.wiley.com/journal/PIP

are the principal defect indicating post-passivation GB recombination activity. In comparison, Fe-rich precipitate decoration was found to play a less significant role. These results point to the importance of efforts to control GB microstructure, including GB type and dislocation density, during the growth and processing of mc-Si solar cells.

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