Compensation of the dangling-bond space charge in amorphous silicon solar cells by graded low-level doping in the intrinsic layer

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The compensation of the dangling-bond space charge in amorphous silicon $p$-$i$-$n$ solar cells by graded, low-level doping in the intrinsic layer is discussed and demonstrated experimentally. Carrier collection in $p$-$i$-$n$ cells without doping indicates that the degraded state space charge is largely positive, and thus that boron doping should be beneficial. Solar cells with linearly decreasing boron doping profiles are shown to yield a homogeneous collection in the intrinsic layer, and a red light conversion efficiency superior to that of undoped cells after light soaking. Also, the optimal doping concentration is shown to be a direct measure of the degraded state defect density.

The electric field in the $i$ layer is essential for the collection of photogenerated carriers in amorphous silicon $p$-$i$-$n$ solar cells. If after light soaking a substantial quantity of dangling-bond defects is present in the $i$ layer, the electric field distribution is distorted because these defects tend to get charged. A positive space charge is expected towards the $p$ side of the solar cell, and negative space charge towards the $n$ side, according to the polarity of the local majority carrier. Such a space charge then leads to a high electric field at the interfaces, and to a reduced electric field in the bulk of the cell. In the low field region, the photogenerated carriers accumulate, and are subject to enhanced recombination. Whereas the actual creation of the defects might be inevitable, the effect of the defects on the electric field can be offset through compensation with a suitable dopant profile. This concept, as proposed previously, \(^1\) offers the potential to increase the stable efficiency of amorphous silicon solar cells without an actual reduction in defect density. While in previous experimental implementations of low-level $i$-layer doping only single-junction solar cells were considered, and no overall gains in stable efficiency were realized, \(^2,3\) the present work recognizes that it is the narrower spectral sensitivity of component cells of multijunction solar cells that offers a new potential of improvements through low-level $i$-layer doping.

$p$-$i$-$n$ solar cells with and without low-level $i$-layer doping were deposited by glow discharge. All solar cells have an $i$-layer thickness of 0.5 μm, and they have transparent back contacts for $n$-side characterization. Carrier collection profiles within the $i$ layer were determined by the bifacial dynamic inner collection efficiency (bifacial DICE) method, \(^4\) based on quantum efficiency (QE) data acquired under bias-light illumination.

Figure 1 shows the carrier collection profile at 0 V external voltage (short circuit) in a $p$-$i$-$n$ solar cell without $i$-layer doping. In the annealed state, the carrier collection is high and uniform over the whole $i$ layer. After light soaking, the carrier collection stays high close to the $p$-$i$ interface, but shows a monotonous decrease throughout the whole $i$ layer to reach its lowest value at the $n$-$i$ interface. This asymmetrical collection after light soaking is in agreement with early stability investigations, \(^5\) where $p$-side illuminated cells were found to be more stable than $n$-side illuminated cells (since then, only $p$-side illuminated amorphous silicon solar cells are employed in general).

The high values of the degraded state collection at the $p$-$i$ interface strongly indicate the presence of positive $i$-layer space charge, because only an increased electric field in this region can explain that the collection does not drop despite the generally enhanced recombination probability in the light-soaked state. At the $n$-$i$ interface there is no indication of an electric field increase, as the collection reaches its lowest value for the whole $i$ layer right at this interface. This asymmetry of the electric field distortion can be understood as the effect of the mobility difference of the two carriers: due to the lower hole mobility, under illumination the hole concentration is higher than the electron concentration over most of the $i$ layer. This was in numerical modeling efforts found to lead to much larger positive defect space charge at the $p$ side than the corresponding negative charge at the $n$ side. \(^5,6\)

It is thus at the $p$-$i$ interface, and only there, that the collection is high enough that the electric field could be reduced to be redistributed to other regions. Transfer of electric field from the $p$-side region towards the back of the $i$ layer requires the introduction of negative space charge. This is achieved by boron doping. $p$-$i$-$n$ solar cells were thus grown incorporating different boron doping profiles in the $i$ layer. The doping was through adding diborane (B$_2$H$_6$) in the 1

![FIG. 1. Carrier collection, measured with the bifacial DICE method, in an undoped $p$-$i$-$n$ solar cell, before and after 100 h of light soaking.](image-url)
ppm range to the silane during the i-layer deposition. At these low concentrations only negligible dopant related changes in defect density were found. The boron doping profiles were designed to be linearly decreasing from the p-i interface, to match the decreasing shape of the presumed positive dangling-bond space charge.

Figure 2 shows the collection distribution in the i layer of a solar cell with linearly decreasing boron doping, starting at 1 ppm at the p-i interface (see Fig. 2, inset). In the annealed state, the collection from the p side of the i layer is strongly reduced. This is due to a reduced electric field in this zone, a consequence of the global field redistribution towards the n side of the cell. Towards the n side, where the electric field is supposedly higher than in an undoped cell, collection is not affected by the boron doping and stays close to unity. After light soaking, the collection at the p side is largely recovered. This is understood as the effect of the negative dopant charge being compensated by positively charged light-induced defects, causing the suppressed electric field to increase in this region. In the back half of the solar cell, the collection undergoes some, however small, reduction. In general, the resulting collection of the graded boron doped cell is more uniformly distributed, and, on average, higher than the degraded state collection in the undoped cell (Fig. 1).

Figure 3 shows the conversion efficiencies of graded boron-doped cells under different illuminations as compared to an undoped reference cell, both before and after 400 h of light soaking. Efficiencies are normalized to the performance of the reference cell in the annealed state for each illumination. For AM 1.5 illumination from the p side, boron doping reduces the annealed state efficiency, because the collection at the p side is low. After light soaking, the efficiencies of the graded boron-doped cells are virtually unchanged, indicating a balance between electric field recovery at the p-i interface, and the general increase of recombination. But still, the undoped cell performs better than the graded boron-doped cells, demonstrating the advantage of a high electric field at the p-i interface over a more homogeneous electric field distribution, when one is measuring the conversion of AM 1.5 light incident from the p side. For AM 1.5 illumination through the n layer, only small differences are seen in the annealed state. After light soaking, the graded boron-doped cells, however, do show superior efficiencies, demonstrating how the electric field redistribution towards the n side of the cell enhances the degraded state collection in the n-i interface region.

For the conversion of a homogeneously absorbed light spectrum (red light), which attaches equal weight to the collection from all parts of the i layer, the degraded state efficiency of the 1 ppm graded doped cell is clearly found higher than that of the undoped cell. This confirms the finding of a higher average collection for the 1 ppm doping profile (Figs. 1 and 2), and thus demonstrates for the first time the capability of the defect charge compensation method to improve the stable conversion efficiency of amorphous silicon p-i-n solar cells. The stronger doping concentration (2 ppm) is obviously already past the optimal concentration, and no im-
proved red light conversion is found after light soaking.

The actual criterion for “optimal” doping is that the collection from the $p$-side, which in the annealed state is suppressed by the doping, recovers after light soaking to again reach values close to the average collection in the rest of the $i$ layer. Otherwise, if substantial parts of the $i$ layer at the $p$ side still show a suppressed collection after light soaking, those inactive regions might as well be removed from the $i$ layer. Figure A shows the normalized $p$-side short wavelength collection for the different solar cells used in this study, before and after light soaking. Clearly, only up to a certain doping concentration can the $p$-side collection be recovered after light soaking. As the doping is further increased (2 ppm), no recovery is observed, i.e., the electric field is overcompensated. Knowing the density of negative charge due to active dopants, the maximal boron doping at which complete collection is still recovered can be used as a measure for the density of light-induced defects present in the $i$ layer. This method of defect evaluation has the advantage that it is based on the direct comparison of dopant charge and defect charge, and thus does not require a calibration via another physical effect. Figure 4 thus implies a defect density in the range between $2 \times 10^{16}$ (1 ppm) and $4 \times 10^{16}$ cm$^{-3}$ (2 ppm) (based on a charge density of $2 \times 10^{16}$ cm$^{-3}$ per 1 ppm of B$_2$H$_6$ in silane, as previously determined for the boron doped materials used in this study). This result might indicate that the actual range of equilibrium (“stabilized”) defect densities in $p$-$i$-$n$ solar cells at one sun illumination is significantly lower than what is typically found in uniform amorphous silicon layers after high intensity light soaking.

With their enhanced stable conversion efficiency for homogeneously absorbed red light, $p$-$i$-$n$ cells with graded boron doped $i$ layers have the potential to increase the stable efficiency of double-stacked amorphous silicon solar cells, if employed as the red light converting bottom cell. For single junction cells, a similar improvement appears to be less likely, as the electric field distortion due to the positive dangling-bond charge may actually be overall beneficial in a single junction cell.

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