Amorphous silicon based electronically-coupled upconverters for crystalline silicon solar cells

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Introduction

The electronically-coupled upconverter (ECUC) is a novel concept for harvesting sub-bandgap photons in crystalline silicon solar cells through the impurity photovoltaic effect [1]. Unlike conventional intermediate band approaches [2] in which mid-gap defects/impurities are introduced to the bulk of the device, this approach utilises a wider-band gap upconverter layer (e.g. *a*-Si) situated at the rear of a conventional Si solar cell in which the defects are contained. The band offset between the upconverter and the Si-bulk injects sub-band gap photocarriers generated in the upconverter into the base whilst isolating carriers generated in the base from entering the upconverter, allowing a net gain in carriers. The working principles of the ECUC solar cell is shown in Figure 1 (a) using an a-Si based ECUC layer as an example. Note that unlike the conventional intermediate band solar cell shown in Figure 1 (b), the carriers generated in the n- and p-regions do not interact with the defects in the a-Si ECUC layer. It has been shown in a recent first-principles study that a 37.4% maximum efficiency can be expected from a-Si/Si ECUC solar cells [3].

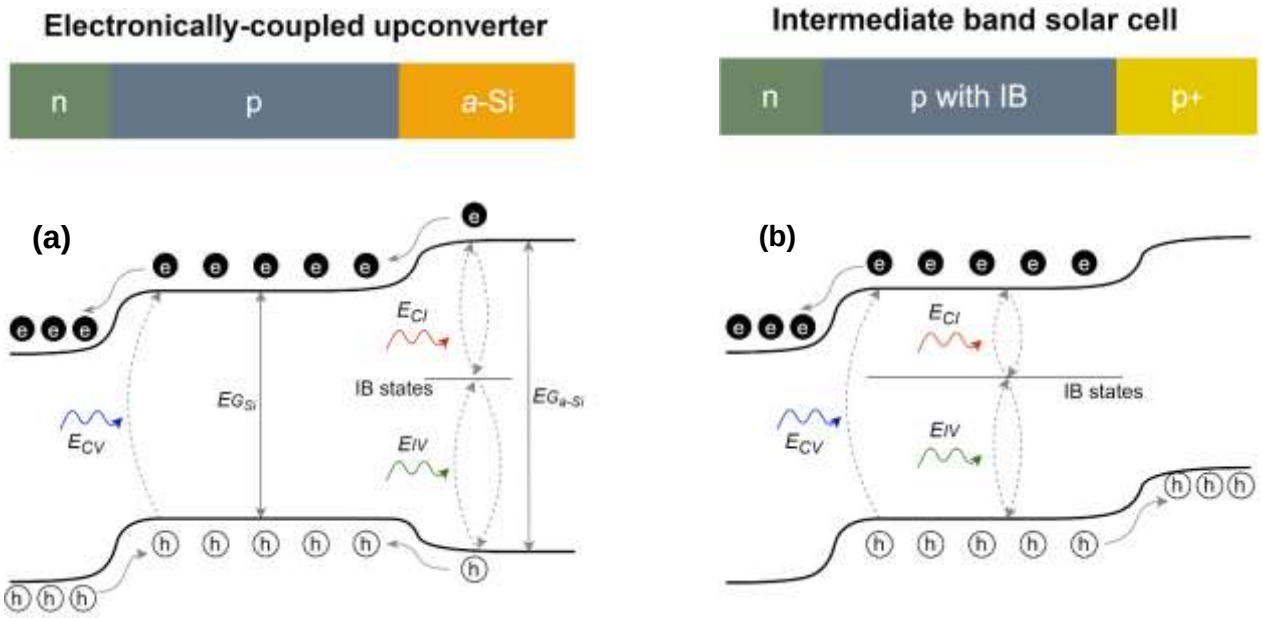

Figure 1. Schematics showing the working principles for (a) an electronically coupled upconverter (ECUC) based on a-Si situated at the back of a conventional Si solar cell, where the mid-gap states are confined to the a-Si layer. The carriers generated from sub-bandgap photons in the a-Si layer are injected into the bulk p-type layer due to the band offset between the a-Si and the p-type bulk; (b) a conventional n/p-IB intermediate band Si solar cell. The p-region of the solar cell contains mid-gap states that enable sub-bandgap photons (E_{CI} and E_{IV}) to be absorbed and converted into carriers.

In this contribution, we describe our recent experimental efforts to create ECUC layers based on intrinsic a-Si:H films, since they are already widely implemented on Si solar cells for their excellent passivation qualities [4], [5]. The mid-gap states are introduced into a-Si via ion implantation of intrinsic (i.e. Si atoms) and extrinsic (i.e. Au atoms) defects. While *a*-Si ECUC layers containing ion-implanted defects have previously been shown to absorb at sub-band gap wavelengths [6], it remains to be seen whether extra sub-bandgap photocarriers can indeed be generated and extracted from the a-Si layers. Herein, we use a range of different implantation conditions to control the type and concentration of defects in the *a*-Si. We study the impact of ion implantation on the carrier lifetime in *a*-Si layers by measuring both the band-to-band photoluminescence signal from the a-Si layer and time-resolved photoluminescence.

Experimental

To prepare the ECUC samples, double-side-polished Cz (100) Si wafers (boron doped,1-10 Ω-cm) first underwent saw damage removal and RCA cleaning before nominally 120-nm-thick intrinsic a-Si:H films were deposited with PECVD on one side. To minimise interference effects in optical absorption measurements, the backside of the wafers was chemically textured using a TMAH-based texturing solution then deposited with an anti-reflecting SiNx film. $^{28}Si^-$ and $^{197}Au^-$ ions were implanted into the a-Si layer at various doses (ranging from 1×10^{14} ions/cm^2 to 5×10^{15} ions/cm^2) at 24 keV and 80 keV respectively, at three implantation temperatures (79K, 300K, 523K). These implantation energies were chosen for each species such that the implantation range was fully confined to the a-Si layer.

Optical absorption measurements were performed using the PerkinElmer NIR-Vis-UV spectrophotometer. The extent of non-radiative recombination in the a-Si layers was monitored by steady-state micro-photoluminescence (u-PL) measurements with a modified confocal Horiba LabRam tool with a 532 nm laser at 79K. The minority carrier lifetime in the a-Si layers was measured with a time-resolved photoluminescence (TRPL) set-up at 8K using an excitation wavelength of 522 nm, as detailed in Ref. [7].

Results and Discussion

As shown in Figure 2 (a), an enhancement in sub-bandgap absorption (up to ~5% absolute at 1200 nm) was observed in samples implanted with Si at 24 keV at room temperature (300K), although the magnitude of the absorption did not seem to scale with the implanted dose. As Si ions are not expected to introduce impurity-induced defect levels in a-Si, the enhanced sub-bandgap absorption is hypothesized to result from structural damage in the a-Si structure that is to be expected from the ion implantation process. Indeed, steady-state u-PL measurements shown in Figure 2 (b) reveal that the ~900 nm a-Si peak reduces with increasing implantation energy, suggesting an increase in the non-radiative recombination activity within the film. This is further supported by TRPL results (not shown) where the a-Si layers show a decrease in lifetime with increasing Si implantation dose.

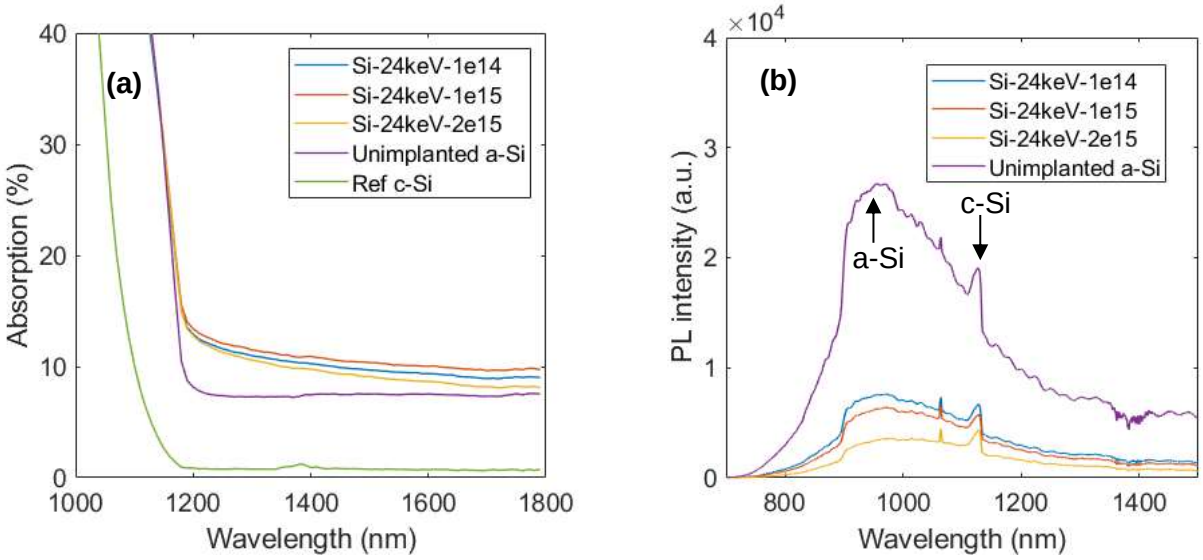

Figure 2 (a) Sub-bandgap absorption and (b) PL spectra of a-Si containing different doses of implanted Si, measured at 79K.

We next investigated the possibility of incorporating *extrinsic* defects (rather than structure related intrinsic defects, as is the case with the Si implanted samples) into the a-Si layer by implanting Au ions into the a-Si layer. The reason for choosing Au as the impurity species is twofold. First, with an atomic mass of 197, Au-ions are much heavier than Si-ions (atomic mass 28) and thus are expected to induce more significant structural damage to the a-Si layer, potentially allowing for more enhancement in sub-bandgap absorption. Secondly, it is well known that Au-induced mid-gap centres exist in c-Si [8], which have recently been shown to facilitate sub-bandgap absorption in Au-hyperdoped Si [9]. The samples implanted with Au at 300K (denoted '300K-Au samples') and at an elevated temperature of 523K (denoted '523K-Au samples') both exihibit a similar degree in sub-bandgap absorption as the Si-implanted samples (data not shown). However, while the RT-Au samples, showed a similar decrease in radiative recombination (i.e. increase in non-radiative recombination) with increasing Au dose as the 300K-Si samples (Figure 2 (a)), it is interesting to see that the 523K-Au samples did not exhibit the same trend. Instead, as shown in Figure 2(b), for samples implanted at 523K, the PL signal in the a-Si part of the spectrum remained consistent for all Au doses ranging from 5×10^{14} ions/cm^2 to 4×10^{15} ions/cm^2.

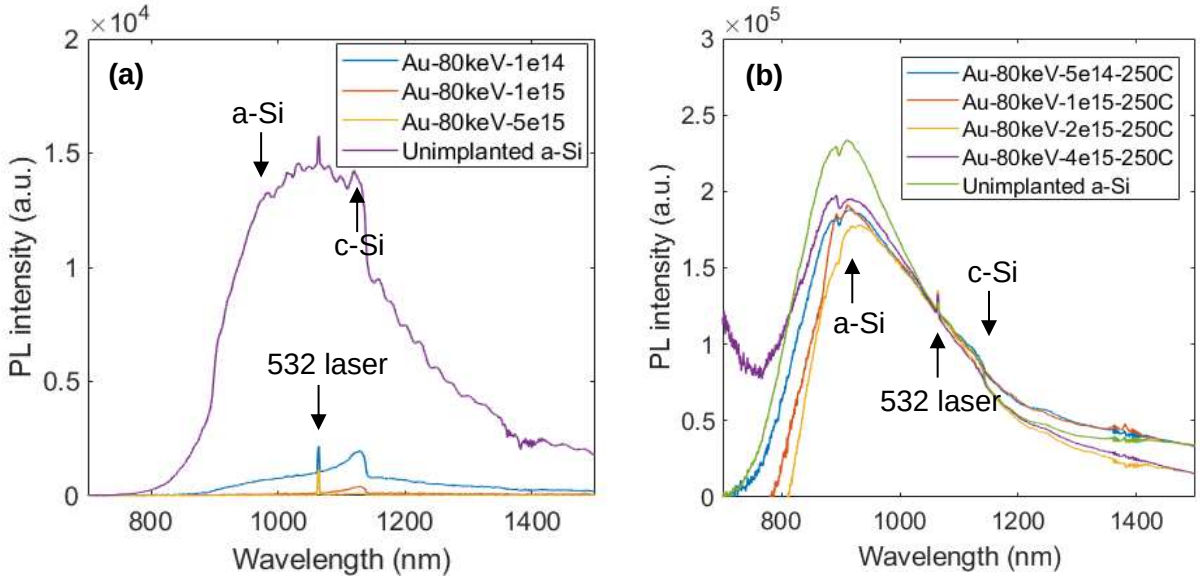

Figure 3 PL spectrum for a-Si implanted with Au at (a) 300K and (b) 523K at different doses.

To quantify the change in the carrier lifetime in the a-Si layers, we normalised the a-Si PL signal by dividing integrated count in the a-Si region by that in the c-Si region. This quantity is then juxtaposed with the carrier lifetime measured from TRPL. As seen in Figure 4, for the 300K-Au samples, both the normalized PL and a-Si lifetime decreased with Au dose, confirming that the decrease in the a-Si PL signal is due to decrease in the a-Si lifetime. At the highest Au dose of 5×10^{15} ions/cm^2, the a-Si lifetime as measured by TRPL has reduced to less than 0.1 ns from ~1 ns (unimplanted). However, for the 523K-Au samples, the a-Si lifetime remained consistently > 2 ns (unimplanted sample has an a-Si lifetime of 2.3 ns). We note that implanting Si at an elevated temperature was not able to produce the same high a-Si lifetime. As it is known that implantation at an elevated temperature may encourage the incorporation of impurities into fourfold-coordinated ('substitutional') positions in the a-Si network [10], [11], the enhancement of sub-bandgap absorption observed in the 523K-Au samples could potentially be related to impurity levels associated with the Au atoms themselves instead of structural damage associated with ion implantation. Furthermore, the annealing effect associated with the elevated temperature during implantation may have repaired some of the structural damage, thereby improving the a-Si lifetime. However, further investigation is required to fully elucidate the mechanism for the sub-bandgap absorption observed.

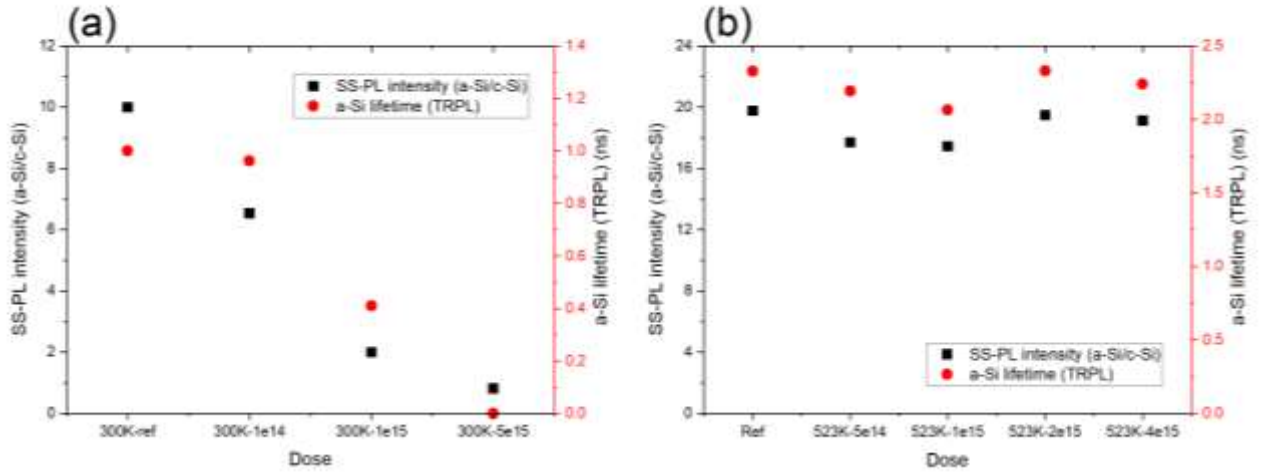

Figure 4 Normalized steady-state PL intensity from the a-Si layer and a-Si lifetime measured from TRPL for (a) 300K Si-implanted samples and (b) 523K Au-implanted samples. We estimate a 10% error in both the normalized PL signal and a-Si lifetime measurements.

Conclusions

In this contribution, we studied ion implanted defects as a means to fabricate an a-Si based ECUC film. While an enhancement in sub-bandgap absorption is observed in samples implanted with both Si (implanted at 300K and 523K) and Au (implanted at 300K), these samples exhibit a decrease in the a-Si lifetime with increasing implantation dose, presumably due to structural damage caused by ion implantation. However, implanting Au at an elevated temperature of 523K appeared to have minimised the reduction in a-Si lifetime whilst giving rise to a similar enhancement in sub-bandgap absorption. These early results suggest that impurity-induced mid-gap levels in a-Si are a more promising platform for ECUC applications than those associated with structural defects (such as those introduced by Si-implantation). More comprehensive work is under way to further understand and parameterize such a-Si based ECUC materials.

References

[1] N.-P. Harder and D. Macdonald, “Electronic up-conversion: a combination of the advantages of impurity photovoltaics and (optical) up-conversion,” 2005, doi: 10.1109/pvsc.2005.1488081.

[2] A. Luque and A. Martí, “Increasing the Efficiency of Ideal Solar Cells by Photon Induced Transitions at Intermediate Levels,” *Phys. Rev. Lett.*, vol. 78, no. 26, pp. 5014–5017, 1997, doi: 10.1103/PhysRevLett.78.5014.

[3] E. Z. Zhang and J. J. Krich, “Efficiency limits of electronically coupled upconverter and quantum ratchet solar cells using detailed balance,” *J. Appl. Phys.*, vol. 217, 2020, doi: 10.1063/5.0005416.

[4] K. Yoshikawa *et al.*, “Silicon heterojunction solar cell with interdigitated back contacts for a photoconversion efficiency over 26%,” *Nat. Energy*, 2017, doi: 10.1038/nenergy.2017.32.

[5] M. Schaper, J. Schmidt, H. Plagwitz, and R. Brendel, “20.1%-efficient crystalline silicon solar cell with amorphous silicon rear-surface passivation,” *Prog. Photovoltaics Res. Appl.*, 2005, doi: 10.1002/pip.641.

[6] D. MacDonald, K. McLean, P. N. K. Deenapanray, S. De Wolf, and J. Schmidt, “Electronically-coupled up-conversion: An alternative approach to impurity photovoltaics in crystalline silicon,” *Semicond. Sci. Technol.*, 2008, doi: 10.1088/0268-1242/23/1/015001.

[7] F. Wang *et al.*, “Spatially resolved doping concentration and nonradiative lifetime profiles in

single Si-Doped InP nanowires using photoluminescence mapping," *Nano Lett.*, vol. 15, no. 5, pp. 3017–3023, 2015, doi: 10.1021/nl504929n.

[8] K. Graff, *Metal Impurities in Silicon-Device Fabrication*. Springer Berlin Heidelberg, 2013.

[9] W. Yang *et al.*, "Au-rich filamentary behavior and associated subband gap optical absorption in hyperdoped Si," *Phys. Rev. Mater.*, vol. 1, no. 7, p. 74602, 2017.

[10] G. Muller and G. Grotz, "Reversible and irreversible structural changes in a-Si," *Philos. Mag. B*, vol. 69, no. 2, pp. 177–196, 1994.

[11] G. Muller, H. Mannsperger, and S. Kalbitzer, "Substitutional doping of a-Si- a comparison of different doping mechanisms," *Philos. Mag. B*, vol. 53, no. 4, pp. 257–268, 1985.