



# Laser illumination for manipulation of hydrogen charge states in silicon solar cells

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This Letter investigates the important parameters of illumination for control of hydrogen charge states in p-type silicon solar cells. Through variations in the wavelength and intensity of illumination, evidence is provided for the importance of the neutral charge state of interstitial hydrogen,  $H^0$ , for

the passivation of defects in upgraded metallurgical grade (UMG) silicon. It is shown that through this approach minority carrier lifetimes may be achieved in excess of those realised through previous techniques, resulting in open-circuit voltages ( $iV_{OC}$ ) over 710 mV.

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**1 Introduction** Hydrogen passivation of defects in crystalline silicon has been the subject of investigations for many years. Many recent publications [1–3] focus upon passivation by atomic hydrogen released from dielectric films during high temperature annealing. This has been shown to result in significant increases in the bulk minority carrier lifetime of silicon devices [2, 4]. However, there are many defects which are not effectively passivated during these processes in p-type silicon, including some grain boundaries [2, 3] and metallic impurities [5, 6].

For further improvements in passivation efficacy of a range of defects in crystalline silicon it becomes important to consider the charge states of atomic hydrogen. Recent studies have provided evidence that these charge states are important for hydrogen interaction with a range of defects in p-type silicon, including the boron–oxygen defect and interstitial iron [7–10]. Interstitial hydrogen may exist in three charge states, positive ( $H^+$ ), neutral ( $H^0$ ) and negative ( $H^-$ ) [11].  $H^0$  in particular has several properties that make it attractive for defect passivation. It is a very rapid diffuser and unlike  $H^+$ , which is the dominant charge state in p-type silicon under most conditions, it is not affected by fixed charges or electric fields.  $H^0$  is also highly reactive due to having a single unpaired electron. The main drawback of  $H^0$  is that it may increase the rate of formation of molecu-

lar hydrogen, which is less effective for defect passivation [1, 12].

In a recent publication [13], evidence was presented that altering the relative concentrations of the charge states of atomic hydrogen had a significant influence upon the minority carrier lifetime in p-type UMG silicon. In particular it was shown that illuminated annealing resulted in higher effective lifetimes under conditions where the simulated fractional concentration of the neutral charge state was increased [11].

This Letter explores the effect of different illumination intensities and a longer wavelength of illumination upon this process. These investigations provide evidence as to whether the enhanced defect passivation observed under illumination is attributable to the effect of hydrogen charge states or whether other explanations are more plausible.

It is further shown that through optimisation of temperature and illumination intensity more effective passivation of defects in p-type UMG silicon may be achieved than reported using any previous approach [7].

**2 Experimental details** These experiments used 100% UMG silicon from the PHOTOSIL project, from which ingots and wafers were produced by Apollon Solar [14]. The wafers were chemically etched and cleaned. Fol-

lowing the chemical cleaning a dielectric layer of silicon oxynitride ( $\text{SiO}_x\text{N}_y$ ) was deposited on both sides using remote plasma-enhanced chemical vapour deposition (PECVD) in a Roth and Rau AK400 tool. The wafers were then subjected to a high temperature belt furnace anneal with a peak temperature of 973 K and a total throughput time of 1.2 minutes, with approximately 1–2 s at peak temperature to release atomic hydrogen from the dielectric into the silicon wafer.

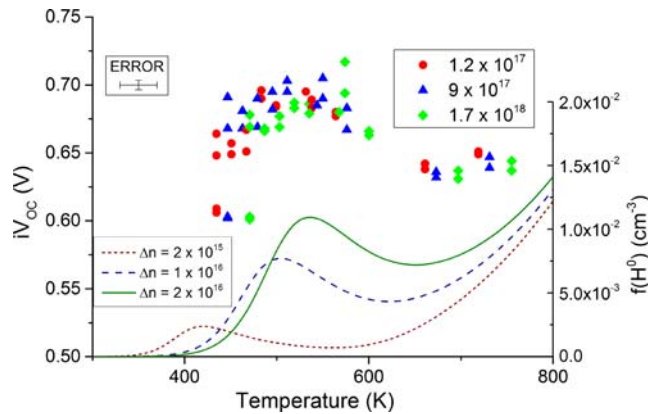
The samples were annealed on a hotplate at temperatures between 400 K and 750 K for 3 minutes before being quenched. The illumination source used was an 808 nm laser with adjustable intensity. Three illumination intensities were used in this work, with photon fluxes of  $1.2 \times 10^{17}$ ,  $9 \times 10^{17}$  and  $1.7 \times 10^{18}$  photons  $\text{cm}^{-2} \text{s}^{-1}$ , as measured using a reference photodiode under illumination. The reflectivity of the samples at this wavelength was measured to be 12.4%. The actual sample temperature was monitored in-situ using an infrared laser detector. To reduce any possible impact of the thermal history and to demonstrate the reversibility of the results anneals were performed in a random order.

The samples were characterized immediately after each thermal treatment in order to minimize degradation of the wafers. These wafers have been observed to degrade under illumination and detailed studies of this effect are currently underway. The effective lifetime as a function of minority carrier density was measured using the Sinton WCT-120 tool and the generalized technique [15]. Additionally photoluminescence (PL) imaging [16, 17] with an illumination intensity of 1 Sun was performed to identify any spatial effects.

### 3 Results and discussion

**3.1 Implied  $V_{OC}$**  A summary of implied open-circuit voltages ( $iV_{OC}$ ) obtained with the 808 nm laser illumination source is presented in Fig. 1. While there is significant variation of results due to differences in processing and wafer resistivity there was a clear trend to increased implied voltages with illuminated annealing between 450 K and 600 K. There is a sharp decline in  $iV_{OC}$  for temperatures below 450 K. For temperatures above 600 K an initial smaller decline is followed by a slight increase in  $iV_{OC}$  with further increase in temperature. Investigation of the injection-level dependent lifetime curves confirmed that there was no significant change in surface recombination and that the observed results were due to changes in the bulk lifetime.

The response of the observed minority carrier lifetime with different light intensities and temperature provides evidence as to whether it is the photons, the minority carrier concentration or the hydrogen charge states that are responsible for the enhanced passivation of defects observed in p-type UMG silicon [13]. If the photons are involved directly then increased illumination intensities should have resulted in higher observed lifetimes at all temperatures. A similar trend would be predicted if the minority carriers



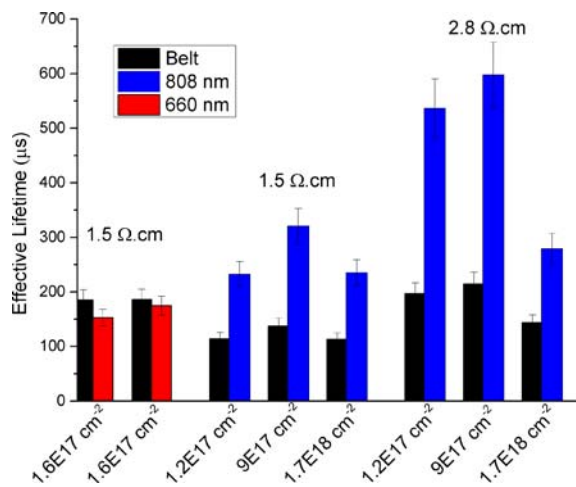
**Figure 1** Implied open-circuit voltages for wafers hydrogenated under 808 nm wavelength illumination. Illumination intensities were  $1.2 \times 10^{17}$  photons/ $\text{cm}^2/\text{s}$  (red circles),  $9 \times 10^{17}$  photons/ $\text{cm}^2/\text{s}$  (blue triangles) and  $1.7 \times 10^{18}$  photons/ $\text{cm}^2/\text{s}$  (green diamonds). The lines represent simulated fractional  $\text{H}^0$  concentrations at excess carrier densities of  $2 \times 10^{15} \text{ cm}^{-3}$  (dark red dashed line),  $1 \times 10^{16} \text{ cm}^{-3}$  (dark blue dashed line) and  $2 \times 10^{16} \text{ cm}^{-3}$  (dark green solid line). Calculated excess carrier densities in these experiments are between  $2 \times 10^{15}$  and  $2 \times 10^{16} \text{ cm}^{-3}$ .

played a direct role in defect passivation. The results in Fig. 1 contradict these predications, even allowing that the poor response at the lowest temperatures may be affected by boron trapping of hydrogen [9, 18].

In contrast, these results show broad agreement with the hypothesis that it is the hydrogen charge states that have the greatest influence. The observed  $iV_{OC}$  in Fig. 1 follow similar curves to the simulated fractional  $\text{H}^0$  concentration for the excess carrier densities involved in these experiments, with a definite peak observable in each. However, the simulations predict an increase in peak fractional  $\text{H}^0$  concentration with increasing intensity which is only weakly reflected in the observed  $iV_{OC}$ .

No correlation is observed with either the positive or negative charge states of hydrogen. However, the charge state of the defect, in conjunction with the hydrogen charge state as observed by Liu et al. [10], may have an impact on the results. More detailed knowledge of the defects involved would be required for greater detail.

**3.2 Comparison with prior processes** A comparison of the lifetimes obtained after the low temperature hydrogenation processes with illumination with those measured after belt furnace firing is highly instructive. In previous work using 660 nm wavelength illumination [13] it was assumed that the high temperature process was likely to give a better response than the low temperature processes due to the higher concentration of the minority charge states of hydrogen as shown in Fig. 1. However, using 808 nm wavelength illumination significantly higher lifetimes have been achieved with the low temperature process than those with the best high temperature process, as shown in Fig. 2.



**Figure 2** Comparison of effective lifetimes for a minority carrier density of  $1 \times 10^{15} \text{ cm}^{-3}$  for individual samples after belt firing and after low temperature hydrogenation. The numbers on the x-axis are the illumination intensities used in photons  $\text{cm}^{-2}$ . Black columns represent the effective lifetime measured after belt firing. Red columns represent the highest effective lifetime measured after hotplate annealing under 660 nm illumination between 475 K and 625 K [13]. Blue columns represent the highest effective lifetime measured after hotplate annealing under 808 nm illumination between 400 K and 750 K. The error bars represent measurement uncertainty.

There are two major reasons that longer wavelength light is considered to be preferable for this process. The first of these is the expectation that longer wavelength light will lead to more uniform generation throughout the bulk. This could be particularly important in non-uniform materials where localised regions of high recombination act to lower minority carrier concentrations in the regions potentially most in need of hydrogen passivation.

Another benefit to using longer wavelength light is the reduction in excess energy lost as heat. Assuming that the photon generation efficiency is the same this will result in a less energy intensive process to achieve the same excess carrier concentration. Furthermore, the reduced irradiation on the wafer will result in a smaller heat gain, allowing more effective control of the temperature profile. This could be of considerable importance if charge state control is attempted during cooling processes after high temperature annealing [7].

While these factors may explain why the longer wavelength of illumination resulted in an increase in bulk lifetime, further explanations are required for why laser hydrogenation outperformed high temperature belt firing. The first of these is the effect on hydrogen passivation of the belt cooling process. It has been previously identified [19] that, in the absence of significant illumination, exposure to temperatures between 473 K and 700 K is likely to result in the rapid reactivation of defects passivated using hydrogen charge state control techniques. Despite the wafers

cooling to temperatures below 473 K over a period of 12 s in the forced cooling section of the belt furnace, it is likely that the inability to control illumination during this cooling process resulted in a non-negligible net reactivation of defects. In contrast wafers from the low temperature process were cooled within a second of the end of the process though quenching. While there was still some net reactivation of defects, the magnitude may be expected to be much smaller than that taking place during cooling subsequent to the belt firing process.

Another factor may be the re-activation of defects during the hydrogenation process itself. The re-activation of defects follows an Arrhenius relation [20] and so reactivation activity will increase exponentially with temperature. The picture is somewhat complicated by factors such as hydrogen release from dielectrics and trapping of hydrogen at dopant impurities, extended defects or other traps. Nonetheless it is reasonable to expect that beyond some critical temperature the ratio of defect passivation and reactivation will decrease with temperature for a constant hydrogen concentration, resulting in an increased equilibrium concentration of active defects.

These effects may also explain to some degree why the highest illumination intensities are not necessarily the most effective. The higher temperatures at which peak  $\text{H}^0$  concentration is reached could result in an increase in reactivation activity either during the process or during cool-down which outweighs the benefits to passivation rate. Further investigation is required to establish confidence in any explanation.

**4 Conclusion** Investigations on the light enhanced hydrogen passivation of defects in p-type UMG silicon have been presented. The results obtained were in broad agreement with the hypothesis that the fractional concentration of  $\text{H}^0$  is a critical parameter in defect passivation in these wafers.

Demonstration of  $iV_{OC}$  over 710 mV on p-type UMG silicon illustrates how this process may be used to passivate a greater concentration of defects than conventional approaches. While investigations into the stability of this passivation are still ongoing, stabilized  $iV_{OC}$  in excess of 690 mV have been demonstrated. If successfully integrated into cell manufacturing processes this could lead to a significant increase in the efficiency of devices manufactured on such substrates.

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