PROGRESS IN PHOTOVOLTAICS: RESEARCH AND APPLICATIONS
Prog. Photovolt: Res. Appl. 2008; **16**:129–134
Published online 5 September 2007 in Wiley InterScience (www.interscience.wiley.com) DOI: 10.1002/pip.775

Research *SHORT COMMUNICATION*

On the Electronic Improvement of Multi-Crystalline Silicon via Gettering and Hydrogenation

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The electronic properties of multi-crystalline silicon must be improved during solar cell fabrication if highly efficient devices are to be made. This work shows how gettering and silicon nitride induced hydrogenation improve three properties: carrier lifetime, interstitial iron concentration, and trap density. Area averaged effective carrier lifetimes less than 10 μs were improved to greater than 60 μs. A tenfold reduction in trap densities was achieved. Photoluminescence images showing the influence processing techniques have on the electronic properties of the silicon are presented. Copyright © 2007 John Wiley & Sons, Ltd.

KEY WORDS: gettering; SiN; mc-Si; hydrogenation

Received 18 February 2007; Revised 14 May 2007

INTRODUCTION

Most solar cells today are produced with a multi-crystalline silicon (mc-Si) substrate. This substrate is inherently defect and impurity rich, but excellent efficiencies can still be obtained.[1–3] This work investigates what improvements are made to the substrate during typical solar cell processing that allows these defect and impurity rich substrates to be manufactured into highly efficient solar cells. Phosphorus gettering has been studied for many years and is widely acknowledged to be vital in transforming the low minority carrier lifetimes of the typical mc-Si wafer.[4,5] Amorphous silicon nitride (SiN) thin films are a newer technology being widely adopted by industry as it strives to create more efficient solar cells. The passivation benefits that annealed SiN can bring are not as well understood as the gettering process and it is the combination of these two passivation effects that this paper addresses.

EXPERIMENTAL DESIGN

A 125×125 mm p-type 1.6 Ωcm (nominal) mc-Si brick was divided into six evenly spaced groups of wafers. Adjacent wafers from these sections were sorted into three sets of samples. The first series of wafers were alkaline etched and set aside as controls. These wafers will hence be referred to as ''As-Cut''. The remaining two sets received an alkaline etch prior to a 30 min double sided phosphorus diffusion resulting in a sheet resistance of $\sim$75 Ω/□. One of the diffused sets was then acid etched to remove the n^+ emitter and thereby enable characterization of the bulk lifetime. These wafers will hence be referred to as ''Gettered''. The second diffused set retained its n^+ emitter and was reserved for characterization post SiN

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deposition and annealing. This series will be referred to as "Gettered + Hydrogenated". An industrial PECVD SiN film was deposited on all wafers using a Roth&Rau SiNA. System diagrams and descriptions of similar systems can be found in the literature.[6] "Gettered + Hydrogenated" samples were then annealed in a rapid thermal annealing furnace with peak temperatures of 700°C and 800°C which were held for 3 s. Wafers were then HF dipped to remove the fired SiN film, and acid etched before a fresh SiN was deposited (using an Oxford PlasmaLab 80+ system) to ensure uniform surface passivation. The photoconductance was measured at nine separate points across the sample using QSSPC.[7] Three parameters were studied: trap density, interstitial iron concentration [Fe_i], and effective lifetime (τ_{eff}) at an excess carrier concentration of 1×10^{15}. Photoluminescence (PL) images of the samples were taken under approximately 0·7 Suns illumination intensity.[8]

RESULTS AND DISCUSSION

Carrier trapping is a phenomenon that frequently occurs in lifetime measurements taken at low injection levels on mc-Si substrates. The mechanism by which trapping occurs in mc-Si was explained by Macdonald and Cuevas[9] using a model from the 1950s.[10] Recent work has linked trapping to regions of high dislocation density and poor lifetime[9,11–13,14] and is increasingly being accepted as a good indicator of crystal quality. Recent research[15] indicates that these traps can be passivated by annealing SiN, which is confirmed by our data. Figure 1 shows the influence that processing has on trap density. The shape of the 'as-cut' control data is similar to that seen in the control [Fe_i] data (Figure 2) and is related to the segregation of impurities during the solidification of the Si during casting. Though the distribution of Fe_i and trapping centers across the ingot maybe driven by the same mechanism, it is unlikely that Fe_i is a major trap center. This is illustrated by the large difference in the magnitudes of [Fe_i] and trap density. After gettering we observe a high uniform trap concentration across the length of the brick. It is possible that the high temperatures required for phosphorus diffusion have created more traps, while simultaneously gettering some of the more lifetime degrading fast diffusing impurities such as Fe_i.[16] The gettered and hydrogenated data shown in Figure 1 are an average of measurements taken for both annealing temperatures. Globally we observe a decrease of up to one order of magnitude in the trap density across the

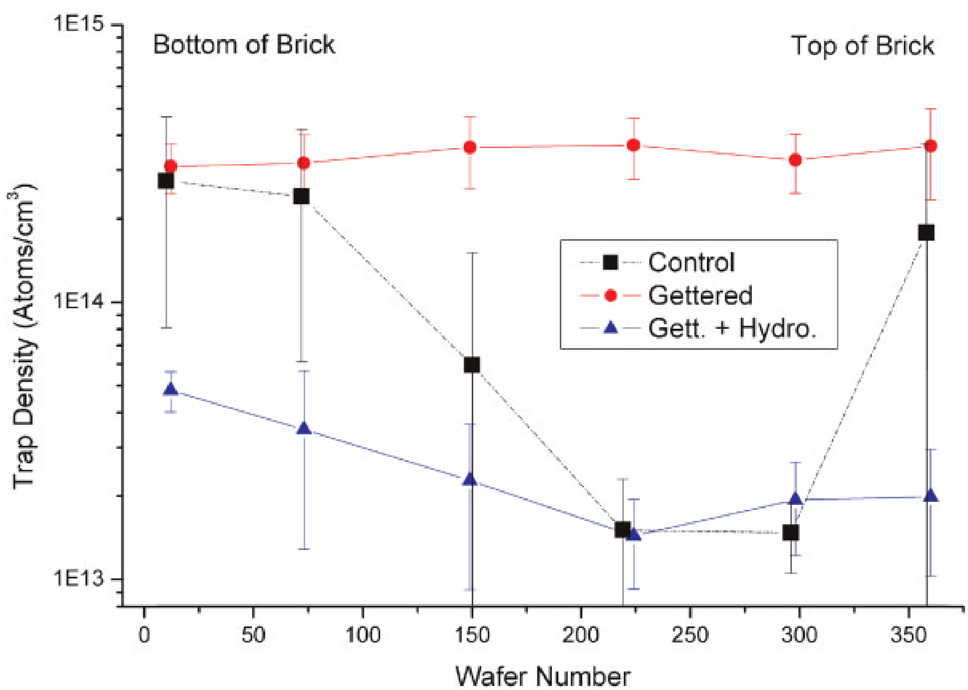

Figure 1. Displays trap density of samples as a function of brick position. Lines are a guide to the eye. Error bars represent the standard deviation of the samples

DOI: 10.1002/pip

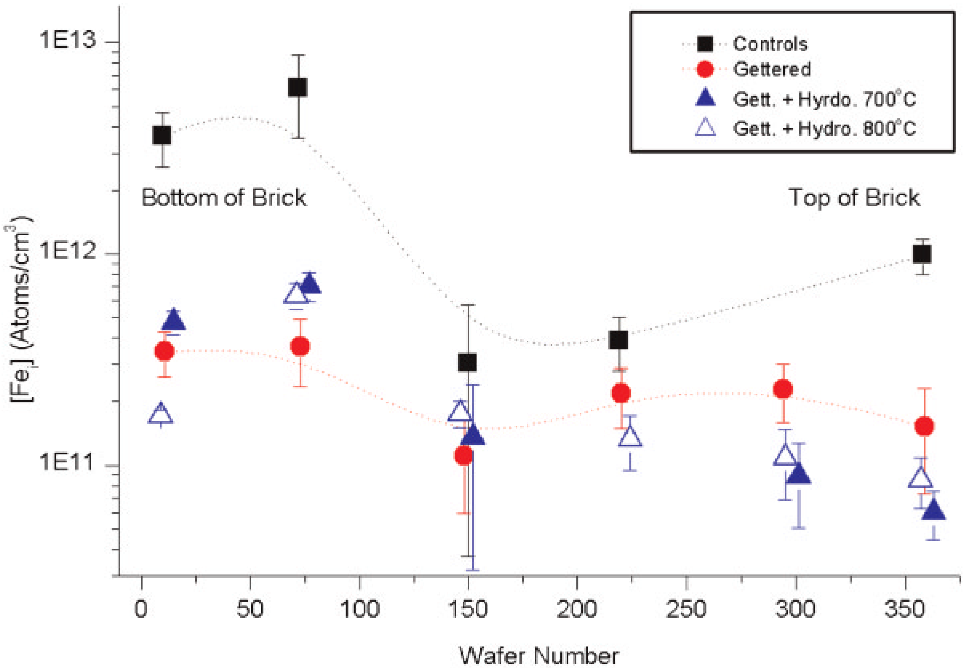

Figure 2. Displays [Fe_i] as a function of brick position. Lines are a guide to the eye. Error bars represent the standard deviation of the samples

ingot after annealing the PECVD SiN. This decrease is attributed to the hydrogenation of the defects which create traps.

Figure 2 displays the reduction in [Fe_i] that processing can achieve on mc-Si wafers. The iron concentrations were determined following the methodology published by Macdonald *et al.*[17] The profile of the control samples is similar to what was observed in the control trap data from Figure 1 and is consistent with previously published results.[18] Gettering has significantly decreased the [Fe_i] at both the top and bottom of the ingot with smaller changes in the middle positions. The ‘‘Gettered + Hydrogenated’’ samples at the top of the brick show a small reduction in the [Fe_i], compared to their ‘‘Gettered’’ only counterparts. It is possible that hydrogenation of the samples has reduced the [Fe_i].[20] However, due to increased errors in the quantitative determination of the [Fe_i] when using this technique with samples of non-homogeneous carrier lifetimes[19] (as is such for mc-Si wafers), this result does not strongly reinforce results published by Azzizi *et al.*[20] and Henze *et al.*,[21] who have shown that SiN induced hydrogenation can passivate the deep level defect that Fe_i produces in the silicon band gap.

Ultimately the most important parameter that determines the efficiency of any solar cell is the carrier lifetime. Figure 3 shows that gettering is effective at improving the τ_{eff} across all regions of the brick. It is interesting to note that the flat region of lifetime at the top of the ingot matches well with the relatively flat [Fe_i] despite the preferential segregation of contaminants during ingot solidification which would increase the concentration of impurities in this region of the brick.[18] This would imply that the gettering was very effective at removing the high impurity concentration expected in this region. In general, the annealed samples display an improved τ_{eff} in the higher regions of the brick due to bulk defect passivation from the annealed SiN. No temperature dependence was observed in the annealed samples as both 700°C and 800°C anneals seem to have increased the τ_{eff} to the same level.

The PL images in Figure 4 are the central 30 × 30 mm regions of neighboring wafers, from the top of the brick, after different processing treatments. The sampling time was kept constant at 1 s. The area averaged (~20 × 20 mm) lifetime displayed with each image is the corresponding QSSPC measurement taken for that region of the wafer. Optical artifacts caused by

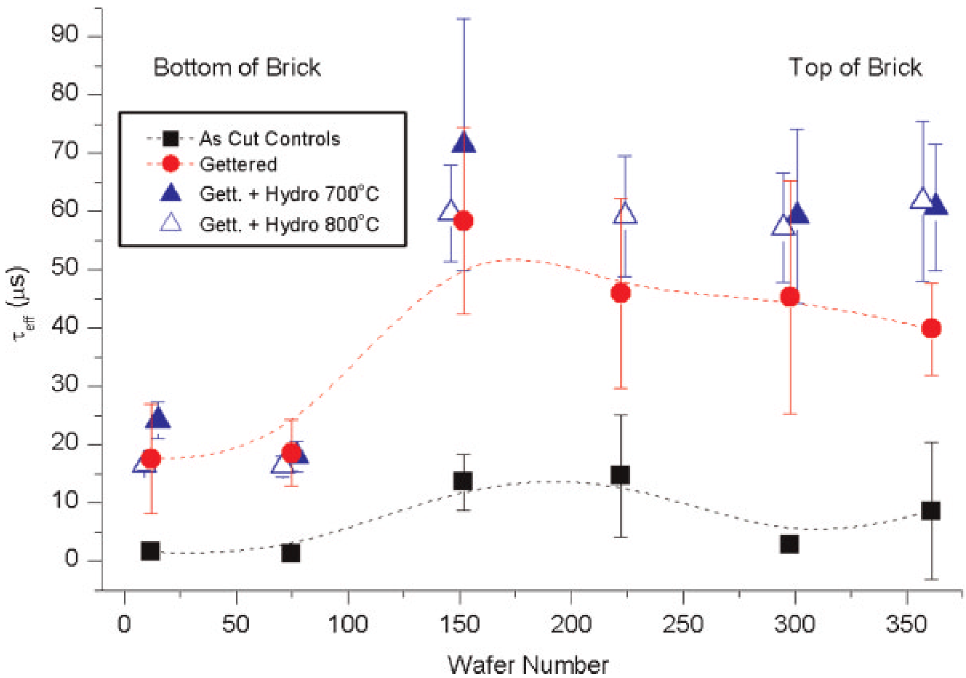

Figure 3. Displays the τ_{eff} as a function of brick position. Lines are a guide to the eye. Error bars represent the standard deviation of the samples

texturing can be ignored as the samples were acid etched, which essentially leaves a planar surface. Figure 4 has been presented as a function of count rate. The PL count rate is directly proportional to the effective lifetime of the wafer. The lower count rate grains observed in Figure 4a are not thought to be affected by their differing grain orientation. If grain orientation did affect the PL images, the darker grains in Figure 4a would be consistently darker in Figure 4b and c, which is not the case.

The image of the as-cut wafer (Figure 4a) is remarkable in its clarity. The sharp definition of each grain, its boundaries, and any scratches on the surface of the wafers (Figure 4a, lower left hand corner) make this image comparable to a black and white photo of the sample. Despite the low τ_{eff}, reflected in the low maximum count rate, the image shows that there are some small differences in the electronic properties of the grains. Though grain boundaries and dislocations are clearly present, they do not significantly effect the

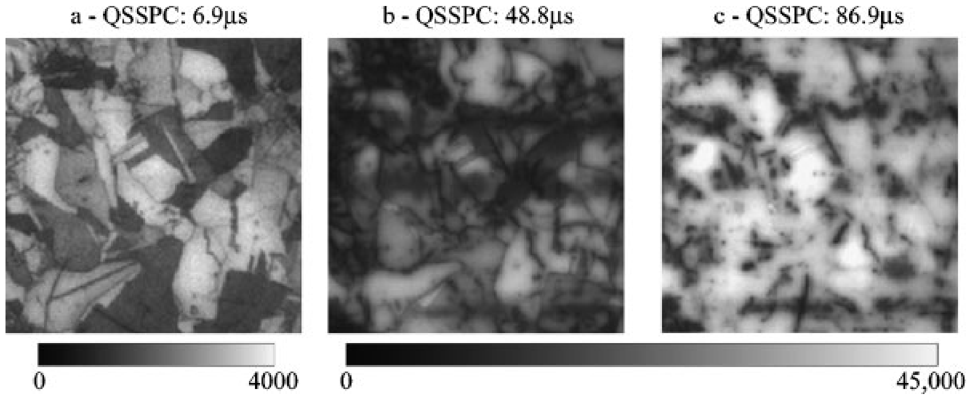

Figure 4. PL images of (a) As-Cut, (b) Gettered, (c) Gettered + Hydrogenated wafers. Color bars represent the maximum count rates of the measurement

DOI: 10.1002/pip

τ_{eff} internal to the grains. After gettering (Figure 4b) higher count rates and hence better global τ_{eff} are measured. However grain boundaries and dislocations have not improved noticeably.[16] Close inspection of grain boundaries bordering a high τ_{eff} grain reveals significant ''bleeding'' compared to the sharper lines observed in Figure 4a. This would imply an increased recombination strength in these areas which is most noticeable in the black regions of high dislocation density.

A possible hypothesis for this is that dislocations have become decorated with impurities during high temperature processing, which the gettering was unable to affect, while the remainder of the grain has been 'cleaned' during the diffusion process. The decoration of these grain boundaries during phosphorus diffusion may explain the increased trapping observed in Figure 1. In Figure 4c, the distinction between grains is significantly reduced due to the passivation of grain boundaries. This reduction of recombination centers has increased the homogeneity of the sample which should translate into an improved open circuit voltage. However, the potential global τ_{eff} of the material has not been drastically increased. This is reflected in Figure 3 where the ''Gettered + Hydrogenated'' samples show an average increase in τ_{eff} of approx. 20 μs compared to their ''Gettered'' counterparts. As researchers have already shown that dislocation density and trap density are linked,[13,14] and that traps can be passivated (Figure 1),[15] Figure 4c demonstrates that SiN induced hydrogenation can passivate grain boundaries and other dislocations[16] which are a primary source of carrier traps.

CONCLUSION

In this work, we have examined how phosphorus gettering and SiN induced hydrogenation can improve the electronic properties of mc-Si. Examination of the [Fe_i] after each processing step has revealed that phosphorus gettering is very effective at removing this fast diffusing impurity from the bulk of the grains. However, our results do not support significant passivation of Fe_i by SiN hydrogenation. Area averaged trapping concentrations and PL imagery after each processing step has revealed that carrier traps maybe caused by grain boundaries and lattice dislocations, which can be effectively passivated with SiN-based hydrogenation. Average τ_{eff} of <10 μs have been improved to >60 μs through the combined use of phosphorus gettering and SiN hydrogenation. The phosphorus gettering has contributed to the improved τ_{eff} by removing τ_{eff} degrading metallic impurities, while the SiN hydrogenation has addressed other recombination sources such as lattice dislocations.

Acknowledgements

The authors would like to thank the Australian Research Council for funding this work. We would also like to thank Florence Chen for helping with the surface passivation of samples.

REFERENCES

1. Schultz O, Glunz S, Riepe S, Willeke G. High-efficiency solar cells on phosphorus gettered multicrystalline silicon substrates. *Progress in Photovoltics* 2006; **14**: 711–719.
2. Tool CJJ, Manshanden P, Burgers AR, Weeber AW. Higher efficiency for thin multi crystalline silicon solar cells by improving the rear surface passivation. In *Proceeding 31st IEEE Conference*, 2005; 1324– 1327.
3. Rohatgi A, Narasimha S. Design, fabrication, and analysis of greater than 18% efficient multicrystalline silicon solar cells. *Solar Energy Materials and Solar Cells* 1997; **48**: 187.
4. Macdonald D, Cuevas A, Ferrazza F. Response to phosphorus gettering of different regions of cast multi-crystalline silicon ingots. *Solid State Electronics* 1999; **43**: 575.
5. Boudaden J, Monna R, Loghmarti M, Muller JC. Comparison of phosphorus gettering for different multicrystalline silicon. *Solar Energy Materials and Solar Cells* 2002; **72**: 381–387.
6. Moschner JD, Henze J, Schmidt J, Hezel R. High-quality surface passivation of silicon solar cells in an industrial-type inline plasma silicon nitride deposition system. *Progress in Photovoltaics* 2004; **12**: 21.
7. Sinton R, Cuevas A. Contactless determination of current–voltage characteristics and minority-carrier lifetimes in semiconductors from quasi-steady-state photoconductance data. *Applied Physics Letters* 1996; **69**: 2510.
8. Trupke T, Bardos R, Schubert M, Warta W. Photoluminescence imaging of silicon wafers. *Applied Physics Letters* 2006; **89**: 044107.
9. Macdonald D, Cuevas A. Trapping of minority carriers in multicrystalline silicon. *Applied Physics Letters* 1999; **74**: 1710.
10. Hornbeck J, Haynes J. Trapping of minority carriers in silicon. I. P-type silicon. *Physical Review* 1955; **77**: 311.

DOI: 10.1002/pip

11. Pohl P, Schmidt J, Bothe K, Brendel R. Mapping of trap densities and energy levels in semiconductors using a lock-in infrared camera technique. *Applied Physics Letters* 2005; **87**: 142104.
12. Schmidt J, Pohl P, Bothe K, Schmiga C, Krain R, Brendel R. Advanced defect characterisation techniques in crystalline silicon based photovoltaics. In *Proceeding 21st European Photovoltaic Energy Conference,* 2006.
13. Schubert M, Riepe S, Bermejo S, Warta W. Determination of spatially resolved trapping parameters in silicon with injection dependent carrier density imaging. *Journal of Applied Physics* 2006; **99**: 114908.
14. Pohl P, Schmidt J, Schmiga C, Brendel Rolf. Defect imaging in multicrystalline silicon using a lock-in infrared camera technique. *Journal of Applied Physics* 2007; **101**(7): 073701.
15. Dekkers H, Carnel L, Beaucarne G. Carrier trap passivation in multicrystalline Si solar cells by hydrogen from SiNx:H layers. *Applied Physics Letters* 2006; **89**: 013508.
16. Rinio M, Kaes M, Hahn G, Borchert D. Hydrogen passivation of extended defects in multicrystalline silicon solar cells. In *Proceedings of the 21st European Photovoltaic and Solar Energy Conference,* 2006.
17. Macdonald D, Geerligs L, Azzizi A. Iron detection in crystalline silicon by carrier lifetime measurements for arbitrary injection and doping. *Journal of Applied Physics* 2004; **95**(3): 1021–1028.
18. Sinton R, Mankad T, Bowden S, Enjalbert N. Evaluating silicon blocks and ingots with quasi-steady-state lifetime measurements. In *Proceedings 19th European Photovoltaic Energy Conference,* 2004.
19. Geerligs LJ, Coletti G, Macdonald D. On accurate and quantitative measurements of iron-concentration in multicrystalline silicon by iron–boron pair dissociation. In *Proceedings of the 21st European Photovoltaic and Solar Energy Conversion,* 2006.
20. Azzizi A, Geerligs LJ, Macdonald D. Hydrogen passivation of iron in crystalline silicon. In *Proceeding 19th European Photovoltaic Energy Conference,* 2004.
21. Henze J, Pohl P, Schmiga C, Dhamrin M, Saitoh T, Yamaga I, Schmidt J. Millisecond area-averaged lifetimes in gallium doped multi-crystalline silicon. In *Proceedings of the 21st European Photovoltaic and Solar Energy Conversion,* 2006.

DOI: 10.1002/pip