

Metallic Impurities in Multicrystalline Silicon

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Secondary Ion Mass Spectroscopy is applied to cast and ribbon-grown multicrystalline silicon in an attempt to discover the major metallic impurities present in these important photovoltaic materials. By analysing a thin diffused layer, in which the impurities are concentrated, the effective sensitivity of the method is increased significantly. The results indicate that Fe and Cr are present in large quantities in cast multicrystalline silicon, while Cu exists in significant amounts in Edge-defined Film-fed Growth ribbon silicon.

1. INTRODUCTION

Multicrystalline silicon (mc-Si) solar cells are playing an increasingly important role in the world photovoltaics market. Although they are slightly less efficient than single-crystal cells, they appear to enjoy an important cost/watt advantage over many single-crystal processes in the current marketplace. However, it seems that to retain this lead, the efficiency of mc-Si cells will need to improve without overly increasing costs. A precondition for this is an improvement in the quality and purity of the material.

Multicrystalline silicon is produced in a number of different forms. The two main types at present are cast mc-Si, which is solidified in large blocks and then sliced into wafers, and ribbon mc-Si, which is grown in thin sheets. The current market share of ribbon technologies is small, but may grow rapidly in the coming years. These mc-Si materials are often characterised by relatively short bulk lifetimes, which are in turn attributed to the presence of defects and impurities in the wafers, particularly metallic ones. This paper uses Secondary Ion Mass Spectroscopy to examine which metal impurities are present in large quantities in cast mc-Si from Eurosolare and ribbon silicon grown by ASE Americas (Edge-defined Film-fed Growth, or EFG silicon). The important question as to what chemical state these metals may be in is also considered.

2. LOSSES IN MULTICRYSTALLINE SILICON CELLS

When attempting to improve the efficiency of solar cells in production, it is useful to examine the physical source of any losses. For a single-junction silicon solar cell, there are some fundamental loss mechanisms which are unavoidable. Most of these intrinsic losses are related to the energy of the photons not exactly matching the band gap of silicon. Further reductions are caused by radiative and Auger recombination. In concert, these intrinsic processes reduce the maximum attainable efficiency for a non-concentrating silicon solar cell to around 29.8% (Tiedje *et al.*, 1984).

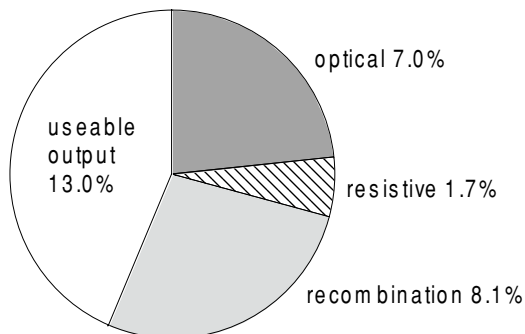


Figure 1. Breakdown of loss mechanisms in a typical commercial cast mc-Si solar cell.

However, commercially produced mc-Si cells do not come close to this upper limit. They typically have efficiencies around 13-14%, as indicated in Figure 1. The figure also indicates the source of these avoidable losses as categorised into three broad groups: optical, resistive and recombination losses. In principle, these losses can be reduced indefinitely, but in practice this faces technical and economic barriers.

Figure 1 represents a standard cast mc-Si cell produced commercially using screen-printed contacts on a heavily doped, homogeneous emitter with a TiO_x anti-reflection

coating (ARC) and aluminium back-surface-field (BSF). Essentially, the optical losses can be modelled in PC-1D (Basore and Clugston, 1998) using the known ARC properties and metal finger dimensions. The resistive losses are estimated from the typical fill factor values, and the recombination losses assumed to make up the difference. As such the results are not exact, but they do serve as a useful guide. Also, it should be noted that it is not possible to simply state that by removing optical losses, the mc-Si cell efficiency would improve by 7% absolute, since the recombination and resistive dynamics would be altered also. Similarly, altering the recombination properties will induce changes in the resistive losses.

The optical section in Figure 1 includes front surface reflection (from metal fingers and the ARC), absorption by the ARC and the rear reflecting surface, and escape of long wavelength light through the front surface (imperfect light-trapping). The resistive component includes bulk, emitter, contact and metal resistive losses. Finally, the recombination section also has a number of contributors, the significant ones being recombination in the bulk, the emitter, and at the front and rear surfaces.

The pie chart clearly indicates that recombination losses in general play an important role in the relatively poor performance of commercial mc-Si cells. Recombination in the bulk of the cell can often form a significant part of this global recombination loss. This then is the context for the work presented in this paper, which attempts to examine possible causes of bulk recombination in mc-Si wafers.

3. EXPERIMENTAL METHODS

Studying impurities in silicon is an intrinsically difficult task, due to the minute concentrations involved. For example, bulk concentrations of interstitial Fe as low as 10^{11}cm^{-3} can significantly effect solar cell performance. Such a concentration represents about one part per trillion atomic, although many impurities are less active than Fe.

One approach is to apply Secondary Ion Mass Spectroscopy (SIMS) to the surface of a wafer that has been phosphorus gettered, with the heavy gettering diffusion remaining. SIMS is well suited to this application since it can analyse impurities to a depth of a few microns, deep enough to traverse most diffusion profiles. The advantage of this technique is that the gettering action concentrates the impurities in the near-surface region, making them more easily detected. This is a critical factor in analysing metallic impurities in silicon, since their bulk concentration is, as alluded to above, typically less than 10^{14}cm^{-3} . Assuming this value, if all the impurities are gettered to the top half a micron in a $300\mu\text{m}$ wafer, the resulting concentration in that thin layer would be $6\times 10^{16}\text{cm}^{-3}$, which is approximately the sensitivity limit of SIMS for many isotopes. The gettering action then 'magnifies' the sensitivity of SIMS by more than two orders of magnitude.

Even so, SIMS of gettered layers is not sensitive enough to measure very small amounts of impurities, and therefore the presence of additional contaminants cannot be ruled out. Nevertheless, the results below are useful in that they reveal the metallic species that are present in the highest concentrations. Both cast and EFG ribbon mc-Si were analysed in this way. During profiling, isotopes of Fe, Cr, Ni and Cu were probed for, since they are amongst the most common found in mc-Si (McHugo *et al.*, 2001).

4. SIMS ANALYSIS OF CAST MULTICRYSTALLINE SILICON

Figure 2 shows the SIMS profile of a $0.9\Omega\text{cm}$ Eurosolare cast mc-Si wafer with a phosphorus gettering layer present at the surface. This was a heavily contaminated wafer, with a bulk lifetime of around $1\mu\text{s}$ before gettering and approximately $2\mu\text{s}$ after gettering. The junction depth of the diffusion is estimated to be approximately $1.2\mu\text{m}$. Since the secondary ion yield varies strongly between different isotopes, the absolute magnitude of the signal is not always an accurate indication of the presence of trace impurities. Rather, a signal that decreases over roughly the same distance as the gettering layer is a more reliable indicator. The plot shows that there is a definite trace of both Cr and Fe in this sample. Ni and Cu however do not appear to be present in sufficient concentrations to be detected using this technique.

To ensure that the observed traces genuinely reflected gettering from the bulk as opposed to surface contamination or other artifacts, a second sample was analysed, but in this case the gettering layer was etched off and the sample given a second heavy gettering diffusion prior to SIMS profiling. Figure 3 shows the results,

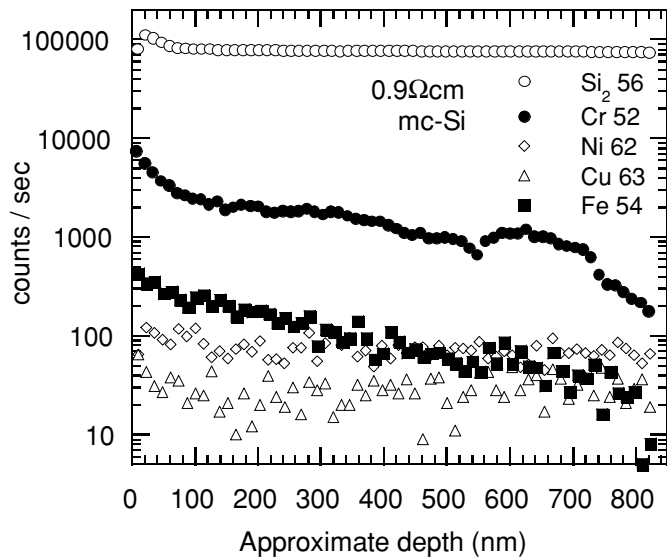


Figure 2. SIMS profile of a Eurosolare mc-Si wafer with a heavily doped gettering layer present. The junction depth is estimated to be approximately $1.2\mu\text{m}$.

methods, although they are less ambiguous. The best SIMS systems available have sensitivities of no better than $5 \times 10^{14} \text{cm}^{-3}$ for the isotopes ^{54}Fe and ^{52}Cr (Wilson *et al.*, 1989). The particular SIMS apparatus at ANU has a bulk sensitivity limit considerably worse than this (at least an order of magnitude), but for our current purposes we shall assume these optimistic values to obtain lower bounds. Since the ^{54}Fe trace in Figure 2 indicates concentrations not far above the noise level, we may assume a minimum concentration of $5 \times 10^{14} \text{cm}^{-3}$ for ^{54}Fe over the approximate junction depth of $1\mu\text{m}$. As stated above, the observed trace may be considerably further above the *real* noise limit, meaning the actual concentration would be greater. This implies a lower bound on the distributed ^{54}Fe concentration throughout the bulk of the $300\mu\text{m}$ wafer of $2 \times 10^{12} \text{cm}^{-3}$. Considering that the natural abundance of ^{54}Fe is 6%, this in turn suggests a minimum total Fe concentration of around $3 \times 10^{13} \text{cm}^{-3}$.

The profile for ^{52}Cr is approximately an order of magnitude higher than that for ^{54}Fe . However, considering that the relative abundance of this isotope is 52%, also an order of magnitude higher, the resulting minimum Cr concentration when distributed throughout the bulk is again around $3 \times 10^{13} \text{cm}^{-3}$. It should be stressed once more that this is a very optimistic lower bound.

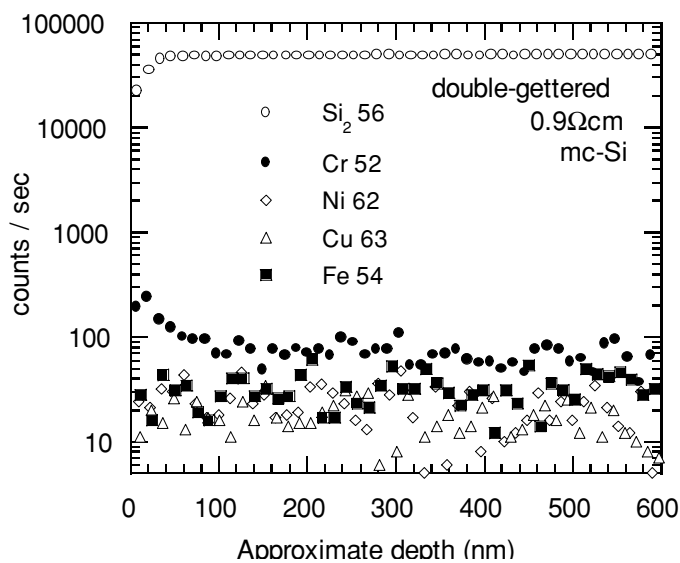


Figure 3. SIMS profile of a Eurosolare mc-Si sample that was gettered twice, the second heavily doped gettering layer remaining during SIMS analysis.

which suggest that the concentration of all four metallic species dropped or remained below the detection limit, as expected.

It is possible to estimate a lower bound on the total Fe and Cr concentrations by considering the sensitivity limit of SIMS for the isotopes in question. The profiles of the double-gettered sample in Figure 3 can be considered as upper bounds on the noise levels for the impurities. Considering that there may be some impurities still present in the diffused region of the double-gettered sample, it is possible that the actual noise levels are lower than this. In the single-gettered wafer, ^{54}Fe occurs at concentrations slightly above this apparent limit, while for ^{52}Cr the signal is considerably higher.

The sensitivity limit of SIMS is not as low as electronic techniques such as Deep level Transient Spectroscopy or lifetime-based

4.1. Chemical State of the Fe and Cr

The recombination activity of the impurities depends critically on their chemical state. Therefore, an important question to consider is in what form are the Fe and Cr atoms present? If present as interstitial atoms, then they can be expected to form pairs with the boron dopant atoms, namely FeB (Zoth and Bergholz, 1990) and CrB (Mishra, 1996) pairs. Fortunately, if the concentration of Fe or Cr is known, it is possible to calculate the bulk lifetime that would result if the metal atoms were present either interstitially or as dopant pairs. These results can be compared with the pre-gettering lifetime of $1\mu\text{s}$ measured in these wafers. The lifetime calculation is

performed using the well-known Shockley-Read-Hall formula (Blakemore, 1962). To do this, the energy levels and electron and hole capture cross-sections σ_n and σ_p for each type of recombination centre are required. These are taken from the literature and are given in Table 1.

Table 1. Energy levels and capture cross-sections for Fe and Cr related recombination centres.

Recombination centre	Energy level (eV)	σ_n (cm ⁻²)	σ_p (cm ⁻²)	Source
Fe _i	E _v +0.38	5×10 ⁻¹⁴	7×10 ⁻¹⁷	(Istratov <i>et al.</i> , 1999)
FeB acceptor	E _c -0.23	3×10 ⁻¹⁴	2×10 ⁻¹⁵	(Istratov <i>et al.</i> , 1999, Macdonald <i>et al.</i> , 2001)
Cr _i	E _c -0.22	2.3×10 ⁻¹³	1.1×10 ⁻¹³	(Mishra, 1996)
CrB	E _v +0.27	1.4×10 ⁻¹³	1×10 ⁻¹⁴	(Conzelmann <i>et al.</i> , 1983, Mishra, 1996)

If we assume a value of 3×10¹³cm⁻³ for the Cr concentration, as calculated above, interstitial Cr and CrB pairs present at these levels would cause the bulk lifetime to be 0.02 and 0.04μs, respectively, at an excess carrier concentration of 10¹⁵cm⁻³. These values are much lower than those actually measured in such non-gettered mc-Si wafers. Hence, it seems that the vast majority of the Cr present must occur in some other, more benign, form.

In a similar manner, assuming a total Fe concentration of 3×10¹³cm⁻³ results in bulk lifetimes of 3μs and 0.6μs for interstitial Fe and FeB pairs respectively. These results suggest that either of these centres *may* provide a plausible explanation for the observed lifetimes. However, it was found that the injection-level dependence of the measured lifetime did not correspond well with those predicted for interstitial Fe or FeB pairs. Furthermore, if Fe were present in these forms, it should be possible to observe a change in lifetime after a 200°C anneal, which serves to break up the FeB pairs (Zoth and Bergholz, 1990). Despite numerous attempts, such behaviour was not observed in these samples.

The results then imply that both Fe and Cr are mainly present in non-interstitial forms. It seems most likely that the high concentrations of these metals reside almost exclusively as precipitates in the wafer bulk. Since each precipitate may contain many such metal atoms, the total density of centres is greatly reduced, meaning that even if the recombination activity of each precipitate is large, the resulting impact on the bulk lifetime will be lower than if the metals occurred on interstitial sites. Such precipitates have previously been observed in cast mc-Si (McHugo *et al.*, 2001).

5. SIMS ANALYSIS OF EFG MULTICRYSTALLINE SILICON

Figure 4 shows a similar SIMS profile for an EFG wafer with the gettering layer intact. The traces for Fe and Cr are inconclusive, because they extend far beyond the gettering layer. However, the Cu trace is more significant, and is most likely due to gettering from the bulk. Once again, the gettering diffusion depth is estimated to be 1.2μm, in good agreement with the observed Cu profile. By comparison with profiles from samples of known Cu content, the results suggest an approximate equivalent Cu surface dose of 10¹³-10¹⁴cm⁻², corresponding to a bulk concentration of 3×10¹⁵-3×10¹⁶cm⁻³. These are very high metal concentrations, and suggest that the recombination strength of the Cu centres, whether in the form of precipitates, substitutional or interstitial Cu, is relatively low.

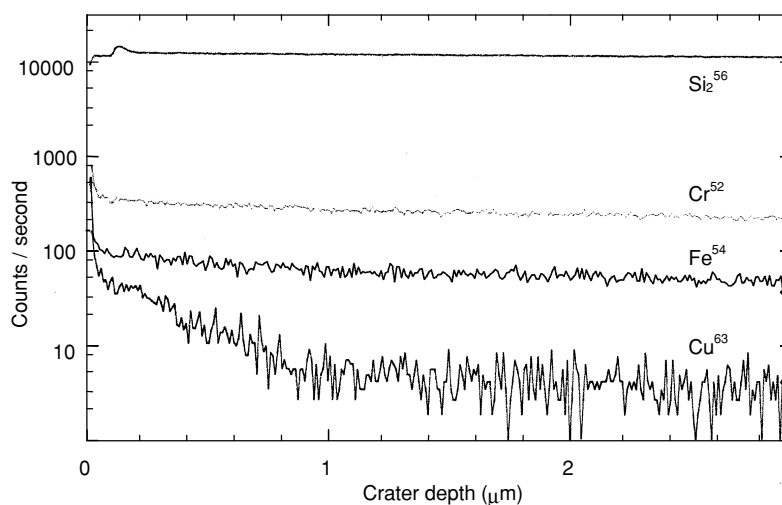


Figure 4. SIMS profile of an EFG mc-Si wafer with the phosphorus gettering layer still present.

Previous studies of the effect of Cu contamination have indeed shown that, at least in p-type silicon, Cu produces relatively weak recombination centres. In fact, work by Naito and

Nakashizu (Naito and Nakashizu, 1992) revealed that for surface doses of the order 10^{13} - 10^{14} cm⁻², Cu related centres were about 2 orders of magnitude weaker than was the case for Fe. Hence it seems plausible that the high levels of Cu found in the EFG material could be responsible for the low lifetimes before gettering. Unfortunately, there is currently little consensus on values for energy levels and capture cross-sections of Cu related recombination centres, making it impossible to model their impact on lifetimes using SRH theory, as was done above for Fe and Cr. Therefore, it is only possible to state that Cu may be at least partly responsible for the low as-grown lifetimes in EFG material, which are typically around 1 μ s.

6. CONCLUSIONS

SIMS analysis of gettered layers has revealed relatively large concentrations of Fe and Cr in cast mc-Si, and Cu in EFG ribbon silicon. The Fe and Cr found in the cast material appears to be present mostly as precipitates, and their recombination activity is uncertain. The discovery of large amounts of Cu in EFG material may be of importance in improving the as-grown lifetime of this promising material, if the source of this contamination can be tracked down and eliminated or reduced.

7. ACKNOWLEDGEMENTS

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8. REFERENCES

- Basore P. A. and Clugston D. A. (1998), *PCID V5.3*, University of New South Wales, Sydney, Australia.
- Blakemore J. S. (1962), *Semiconductor Statistics*, Pergamon Press, Oxford.
- Conzelmann H., Graff K. and Weber E. R. (1983), *Chromium and chromium-boron pairs in silicon*, Appl. Phys. A, 30 169-175.
- Istratov A. A., Hieslmaier H. and Weber E. R. (1999), *Iron and its complexes in silicon*, Applied Physics A, 69 13-44.
- Macdonald D., Cuevas A. and Wong-Leung J. (2001), *Capture cross-sections of the acceptor level of FeB pairs in p-type silicon by injection-level dependent lifetime measurements*, Journal of Applied Physics, June.
- McHugo S. A., Thompson A. C., Mohammed A., Lambie G., Perichaud I., Martinuzzi S., Werner M., Rinio M., Koch W., Hoefs H. U. and Haessler C. (2001), *Nanometer-scale metal precipitates in multicrystalline silicon solar cells*, Journal of Applied Physics, 89 (8), 4282-4288.
- Mishra K. (1996), *Identification of Cr in p-type silicon using the minority carrier lifetime measurement by the surface photovoltage method*, Appl. Phys. Lett., 68 (23), 3281-3283.
- Naito S. and Nakashizu T. (1992), Mater. Res. Symp. Proc., 262 641.
- Tiedje T., Yablonovitch E., Cody G. D. and Brooks B. G. (1984), *Limiting efficiency of silicon solar cells*, IEEE Transactions on Electron Devices, Ed-31 (5), 711-716.
- Wilson R. G., Stevie F. A. and Magee C. W. (1989), *Secondary Ion Mass Spectroscopy: A Practical Handbook for Depth Profiling and Bulk Impurity Analysis*, Wiley Interscience.
- Zoth G. and Bergholz W. (1990), *A fast, preparation-free method to detect iron in silicon*, Journal of Applied Physics, 67 (11), 6764-6771.