Impurities in solar-grade silicon

D. Macdonald* and J. Tan
Department of Engineering, College of Engineering and Computer Science,
The Australian National University, Canberra, ACT, 0200, Australia

ABSTRACT

Unintentional impurities can play a significant role in reducing the efficiency of crystalline silicon solar cells. With the advent of low-cost solar-grade silicon feedstocks, this is likely to remain the case well into the future. The purpose of this paper is to review the most important impurities in directionally-solidified ingot-grown multicrystalline silicon, their chemical states, where they come from, and the most commonly used techniques to detect them.

Keywords: Photovoltaics, silicon, metallic impurities

1. INTRODUCTION

In the past, feedstock for crystalline silicon solar cells has come from leftovers, scraps and off-specification material from the microelectronics industry. However, the photovoltaic market has now outgrown this source of silicon. As a consequence, new forms of low-cost 'solar-grade' silicon are currently being developed. These will form the basis for the future photovoltaic industry, and hopefully lead to significant cost reductions for solar electricity generation. However, these forms of silicon contain greater concentrations of impurities, including metals and unwanted dopants. This paper will outline recent progress in understanding the impact of some of the most important impurities, especially metals, on the performance of solar cells. Ultimately, the aim is to produce impurity tolerance levels for these new sources of solar-grade silicon. This task is complicated by the fact that impurities may occur in numerous different chemical states, for example in precipitates, or as point-like impurities. In addition, the impact of these impurity states may be dramatically different in n- and p-type silicon.

2. IMPURITIES IN SOLAR-GRADE SILICON

Not surprisingly, the type and concentration of impurities present in silicon materials for photovoltaics depends very strongly on the growth technique. At one extreme, today's very pure single-crystal silicon wafers grown by the float-zone method are effectively impurity-free in terms of recombination. Generally, solar cells made with such material are limited by recombination at the surfaces and diffused regions, or by Auger recombination in the base, unless bulk contamination occurs during cell fabrication. Next in line, most Czochralski silicon is also effectively metal-free in terms of recombination, but is prone to the well-known B-O defect.[1] This occurs due to the relatively high levels of dissolved oxygen derived from the quartz crucibles that contain the silicon melt.

Multicrystalline silicon materials made especially for photovoltaics include ingot-grown materials (most commonly directionally-solidified), and sheet and ribbon silicon (grown vertically without a substrate, for example edge-defined Film-fed Growth (EFG) and String Ribbon, or grown horizontally on a substrate, for example Ribbon-Grown Silicon (RGS) and SiliconFilm)[2], as discussed in detail in Ref. 2. These tend to contain a significant number of impurities that derive from the foreign materials (crucible walls and linings, supporting substrates) in direct contact with the molten silicon. Finally, polysilicon thin films formed by crystallising amorphous films deposited on foreign substrates, such as CSG silicon, also contain significant quantities of impurities.[3] In this paper we will focus on directionally-solidified ingot-grown multicrystalline silicon, the most common material for photovoltaics, although the impurities in other solar-grade forms of silicon, and the techniques used to detect them, are often the same as those presented here.[2-4]

The fundamental mechanisms which determine the distribution of impurities in an ingot are segregation and diffusion. Most impurities have segregation coefficients less than unity, meaning they are more soluble in the liquid phase than the solid phase. This leads to higher concentrations in the top of a multicrystalline ingot (where crystallisation proceeds from

*daniel.macdonald@anu.edu.au

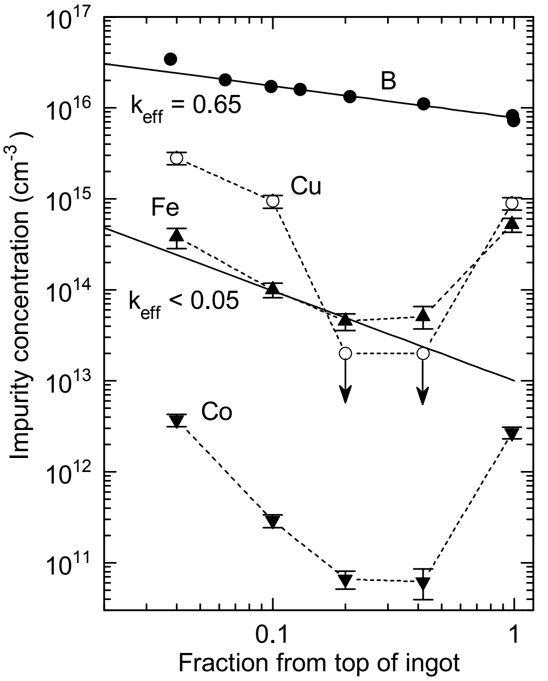

Fig. 1. Concentrations of B, Fe, Co, and Cu as a function of ingot position (fraction from top, hence 0 is the top, 1 the bottom). The straight lines are segregation model fits with k_{eff}=0.65 for B and k_{eff}<0.05 for Fe. From Ref. 6.

the bottom). An exception is oxygen, which has the reverse trend. Shallow dopants tend to have segregation coefficients not much less than unity, leading to relatively gentle increases towards the top of an ingot. Most transition metals, however, have very small segregation coefficients. This in principle allows very effective segregation to the top of an ingot. In practice this is often reduced somewhat by the tendency of structural defects to enhance the incorporation of impurities into the solid phase than would occur otherwise.[5,6]

A feature of ingot-grown multicrystalline silicon is the very long ingot cooling time, tens of hours typically. This allows for a re-distribution of impurities via solid-state diffusion from the original distribution generated by segregation. This is a significant factor in the commonly observed low lifetime regions seen at the bottom and sides of such ingots, although disrupted crystal structure also contributes. Figure 1 shows profiles for some typical impurities in a multicrystalline silicon ingot, taken from Ref. 6, as measured by neutron activation analysis. The segregation towards the top of the ingot is clear in all cases, including boron, which has an effective segregation coefficient k_{eff} not far from unity (0.65), and is a slow diffuser. Solid-state diffusion from the bottom is also evident for the fast-diffusing metals Fe, Cu and Co.

Such data provides strong clues on the source of the metallic impurities in question. It is clear that the metals at the bottom of the ingot have come from the crucible walls and linings. It is also likely that most of the metals found at the top of the ingot have come from the same source. This seems feasible when considering that the silicon charge remains entirely molten for a considerable time before crystallisation begins, allowing impurities from the crucible to dissolve into the melt, which are subsequently segregated to the top during solidification. Note that the peak concentrations at the bottom and top are similar, as is the amount of time available for both dissolution into the melt and solid-state in-diffusion. Note also that the order of concentration of the three metal impurities is similar at the top and bottom (i.e Cu, then Fe, then Co), again indicating that they come from the same source: the crucible (perhaps from previous crucibles if ingot tops and bottoms are recycled).

In the following sections we examine three different categories of impurities in directionally-solidified ingot-grown multicrystalline silicon in more detail: metal impurities; oxygen, carbon and nitrogen; and the shallow dopants.

2.1 Metal impurities

Unwanted metallic impurities are the cause of a large fraction of the total recombination events in solar cells made from materials such as multicrystalline silicon. These metals may be present in a number of different chemical forms, such as point-like (interstitial or substitutional), or in precipitates, which often form at structural defects such as grain boundaries, dramatically increasing their recombination activity.

In directionally-solidified ingot-grown multicrystalline silicon, the most abundant appear to be Fe, Ni and Cu, and to a lesser degree Cr, Co and Mo.[2,4,6-9] Others such as Mn, Ti , Zn and V have also been detected in such materials, although generally at fairly low concentrations.[2,4,9]

Most transition metals occur as interstitial impurities when present in silicon below the solid-solubility limit. Ni, Cu and Co are such rapid diffusers that they almost always completely precipitate out at surfaces or internal defects during cooling after ingot growth or cell processing. Some small fraction of these impurities may remain frozen-in in

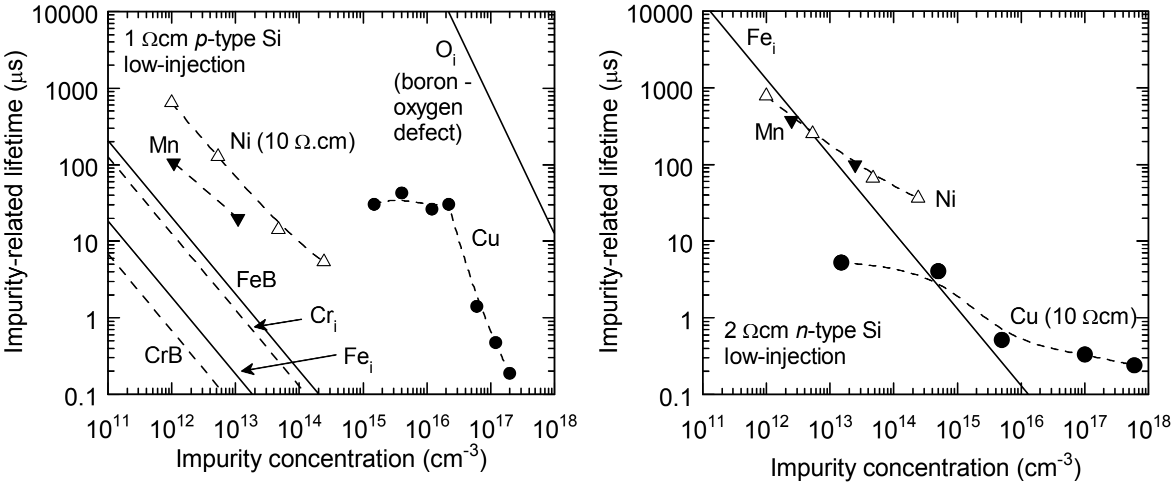

Fig. 2. Left: impurity-related lifetimes in *p*-type silicon. The resistivity is 1 Ωcm (except for Ni, 10 Ωcm), and true low-injection conditions prevail (except for Mn $\eta = 0.1$, Ni $\eta = 0.01$, and B-O$\eta = 0.1$). Right: impurity-related lifetimes in *n*-type silicon. The resistivity is 2 Ωcm (except for Cu, 10 Ωcm), and true low-injection conditions prevail (except for Mn $\eta = 0.1$ and Ni $\eta = 0.01$). Taken from Ref. 14.

substitutional form, but if they do, there is little evidence of their impact in photovoltaic silicon materials.

Impurities with moderate diffusivities, such as Fe, Cr, and Mn, tend to mostly precipitate as well, as shown, for example, by synchrotron-based methods.[2,10] They tend to co-precipitate at the same sites as Ni and Cu, forming alloyed silicides.[2] However, they usually retain a small but detectible fraction in interstitial form after typical high temperature steps, since at a certain temperature they can no longer reach a favourable precipitation site before being effectively frozen-in. For example, approximately 1% of Fe in as-grown mc-Si wafers exists in interstitial from, while the rest is precipitated, mostly at structural defects.[6] Nevertheless, this small interstitial fraction has a significant impact on the overall carrier lifetime.

Fe, Cr and Mn remain very slightly mobile even at room temperature, giving rise to their well-known property of forming pairs with positively-charged ionised dopant atoms such as B, Ga and Al [11]. The ability to easily toggle between the paired and un-paired states, which have different recombination properties, permits very sensitive detection of these interstitial impurities in silicon via carrier lifetime or diffusion length measurements.[12] Like many transition metals, Fe and Cr carry a positive charge when ionised in crystalline silicon. This helps drive the coulombic attraction to the negatively-charged dopant atoms. It also means that they are more attractive as traps to electrons, which in turn leads to greater recombination activity in *p*-type silicon (in which electrons are minority carriers) than in *n*-type silicon.[13] The moderate diffusivity of these impurities at typical processing temperatures means that they can be effectively gettered by phosphorus or aluminium diffusions.

Very slowly diffusing impurities such as Ti, Mo and V remain more evenly distributed during ingot growth, unless originally present as undissolved inclusions in the melt.[2] A larger fraction is likely to remain in interstitial form and un-precipitated than is the case for Fe, Cr and Mn. Nevertheless, they are also detected at precipitates,[2] often in the company of the faster diffusing metals above. Despite having positive charge states in the interstitial form, they do not form pairs with dopant atoms because they are effectively completely immobile at room temperature. Their low diffusivity also means they are impervious to gettering at temperatures and times typically used for device processing.

Naturally, point-like metals in general have greater recombination strength ‘per atom’ than precipitated metal atoms, since the latter are co-located. This highlights the importance of the distribution and chemical state of impurities, rather than simply their total average concentration. It also offers the prospect of defect engineering, in which appropriate treatments could be developed to coax the impurities into their most benign distribution and chemical state. The recombination activity[14] of some common impurities are shown in Figure 2 for both *p*- and *n*-type silicon (taken from Ref. 14).

The challenge in detecting metal impurities in multicrystalline silicon wafers lies in their relatively low concentrations, typically in the range of 10^{10} to 10^{15}cm^{-3}. In some cases mass spectroscopy techniques such as Secondary Ion Mass

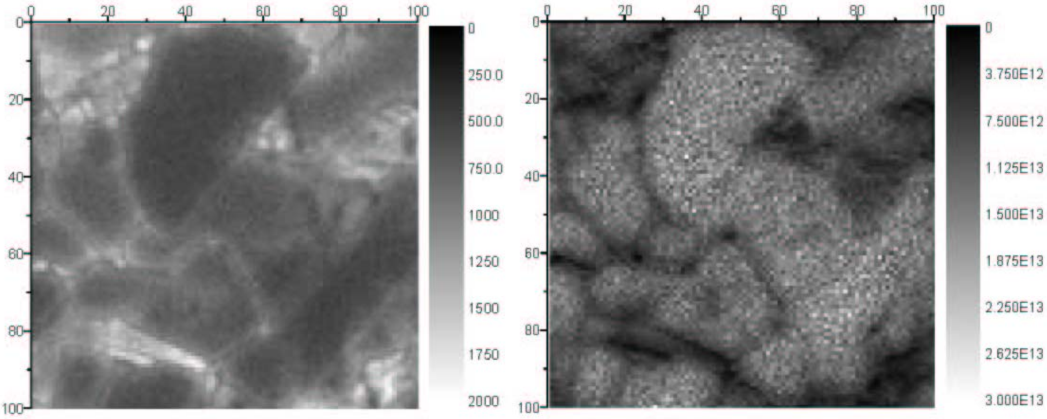

Fig. 3. PL image before pair dissociation (left) of the small region shown in Figure 6 of wafer #69a, and the corresponding iron image (right). The left scale shows the PL count rate, the right scale the iron concentration in units cm^{-3}. The images show a region 17mm in size.

Spectroscopy (SIMS), Glow-Discharge Mass Spectroscopy (GDMS) or Inductively-Coupled Plasma Mass Spectroscopy (ICP-MS), can be used effectively. Generally though, they are only successful for the most heavily contaminated samples, or if the contaminants are concentrated, for example, in the near-surface region via phosphorus gettering. SIMS has been successfully used to reveal the effectiveness of such gettering in removing native impurities in mc-Si such as Fe, Cr, Cu and Ni,[9,15] or, using highly focussed ion beams, for studying impurities segregated to grain boundaries.[16] Such techniques reveal the total concentration of metals, irrespective of their chemical state.

Techniques based on tightly focussed synchrotron radiation have also been successfully applied to metal impurities in mc-Si, and other solar-grade materials.[2,7,8,10] X-ray Fluorescence Spectroscopy (XFS) with a high resolution microprobe (beam size below 1 micron), has been used to detect metals in precipitates, courtesy of their locally high concentrations. Precipitates as small as several tens of nanometres have been detected in this way. This has revealed much about the size and distribution of such precipitates, and also their location in relation to structural defects such as grain boundaries. Applying X-ray Absorption Near-Edge Spectroscopy (XANES) with the same high spatial resolution can reveal the chemical state of such precipitates.

Another technique successfully applied to identifying metals in mc-Si is Neutron Activation Analysis.[4,6] This is more sensitive than the techniques above, but has little capacity for spatial resolution, and can not reveal information about chemical states. The sensitivity is also highly dependent on the target species, and can vary from as low as 10^{10} to above 10^{14} cm^{-3}.

The most sensitive techniques for detecting metal impurities in semiconductors are based on electrical measurements. Deep-Level Transient Spectroscopy (DLTS) can in principle reach detection limits as low as $10^{-4}\times N_{A/D}$. However, it is generally used for detecting point-like impurities, and the presence of precipitates can make the interpretation of the spectra difficult.[17,18] Nevertheless, there have been a number of successful applications of DLTS to solar-grade multi- and poly-crystalline silicon wafers. These have identified, for example, oxygen-related levels and vanadium and chromium impurities in multicrystalline silicon,[19,20] and interstitial Fe and Cr in EFG ribbon silicon[21,22] and in sheet silicon.[23]

Finally, methods based on measuring the carrier lifetime before and after defect transformation can also be very sensitive for certain impurities in *p*-type silicon. The best known case is that of interstitial Fe, detected through diffusion length or lifetime measurements before and after FeB pair dissociation by strong illumination.[12] Detection limits as low as 10^{10} cm^{-3} can be reached in this way. The same approach has been used for interstitial Cr with thermal dissociation,[20,24] and should also work for Mn. In a similar manner, the effective density of B-O centres in oxygen rich Si can be determined before and after defect activation via illumination.[25]

Interstitial Fe ‘maps’ can be made by via point-by-point lifetime measurements before and after FeB pair breaking, as has been done for many years.[26] Recently, lifetime imaging techniques, such as photoluminescence (PL) imaging[27], have become available, which allow very rapid and high resolution lifetime images to be obtained. These can also be used to obtain Fe 'images'. Figure 3 shows an example of such an Fe image from PL images that were taken with a 1 second exposure time. The internal gettering of Fe to the grain boundaries during ingot growth in this multicrystalline wafer is clearly visible.

2.2 Oxygen, carbon, nitrogen and dopant impurities

These three impurities are ubiquitous in silicon materials, but fortunately are quite benign in terms of recombination. An important exception is the well-known B-O defect initially found in Cz silicon, but which also occurs to a lesser degree in mc-Si.[25] Oxygen also forms an active recombination centre with Al.[28] Excessive oxygen can lead to the formation of thermal donors and larger oxygen precipitates.[19,29,30] Interstitial oxygen concentrations are typically in the range of 5-10 ppma near the bottom of a mc-Si ingot, decreasing towards 1-3 ppma at the top.[31] In cases where it has exceeded 10 ppma, significant reductions in carrier lifetime and cell performance were observed.[31] Substitutional carbon concentrations are typically in the range 7-11 ppma.[31] If present in very high concentrations, carbon and nitrogen can form SiC and SiN inclusions within an ingot. These can cause wire breaking during wafering, or create conductive pathways than can potentially produce shunts across the *p-n* junction of a solar cell.

Fourier Transform InfraRed spectroscopy (FTIR) is used to directly detect interstitial O and substitutional C.[32,33] Interstitial nitrogen forms complexes with itself and oxygen which can also be detected by FTIR.[34] Due to their relatively high concentrations, total concentrations of these elements can be detected with mass spectroscopy methods such as SIMS, GDMS or ICP-MS, or also by Auger electron spectroscopy.[16]

Shallow dopants in silicon, such as B, Ga, Al, As and P, are mostly present in substitutional form. They are therefore very slow diffusers, but tend to have high solubility limits compared to interstitial metals. If present in super-saturated concentrations at high temperatures they may form agglomerates or small precipitates.

Shallow dopants form complexes with other impurities to generate important recombination centres, such as the Al-O and B-O defects mentioned above. They also form the stationary part of meta-stable metal-dopant pairs with Fe, Cr, Mn and Co.[11] Dopants are among the most difficult of the impurities to remove during feedstock production, due partly to their high solubility and segregation coefficients. This means that wafers made from new forms of solar-grade silicon feedstock are likely to be compensated to a greater extent than existing material. In principle, it is possible for shallow dopants to act as recombination centres in their own right. Generally this is not considered important since the recombination activity of majority carrier dopants is expected to be very slight, courtesy of their negligible interaction with the minority carrier band. However, compensated *minority* carrier dopant atoms may have significantly greater recombination strength based on their likely charge state.[35] Whether this is sufficient to have an impact in highly compensated material remains an open question.

Dopants are generally present in relatively high concentrations, hence their total concentrations are accessible by mass spectroscopy techniques such as SIMS, GDMS and ICP-MS. The fraction of electrically-active dopants can be inferred, for example, from conductance measurements for bulk concentrations, or from stripping Hall or C-V measurements for the near-surface region.

This work has been supported by the Australian Research Council.

REFERENCES

[1] J. Schmidt and K. Bothe, "Structure and transformation of the metastable boron- and oxygen-related defect center in crystalline silicon", Physical Review B **69**, 024107 (2004).

[2] T. Buonassisi, A. A. Istratov, M. D. Pickett, M. Heuer, J. P. Kalejs, G. Hahn, M. A. Marcus, B. Lai, Z. Cai, S. M. Heald, T. F. Ciszek, R. F. Clark, D. W. Cunningham, A. M. Gabor, R. Jonczyk, S. Narayanan, E. Sauar and E. R. Weber, "Chemical natures and distributions of metal impurities in multicrystalline silicon materials", Progress in Photovoltaics: Research and Applications **14**, 513 (2006).

[3] M. J. Keevers, A. Turner, U. Schubert, P. A. Basore and M. A. Green, "Remarkably effective hydrogenation of crystalline silicon on glass modules", in Proceedings 20th European Photovoltaic Solar Energy Conference, (Barcelona, Spain, 2005).

[4] A. A. Istratov, T. Buonassisi, R. J. McDonald, A. R. Smith, R. Schindler, J. A. Rand, J. P. Kalejs and E. R. Weber, "Metal content of multicrystalline silicon for solar cells and its impact on minority carrier diffusion length", Journal of Applied Physics **94**, 6552 (2003).

[5] A. A. Istratov, W. Huber and E. R. Weber, "Experimental evidence for the presence of segregation and relaxation gettering of iron in polysilicon layers", Applied Physics Letters **85**, 4472 (2004).

[6] D. Macdonald, A. Cuevas, A. Kinomura, Y. Nakano and L. J. Geerligs, "Transition metal profiles in a multicrystalline silicon ingot", Journal of Applied Physics **97**, 033523 (2005).

[7] S. A. McHugo, A. Thompson, I. Perichaud and S. Martinuzzi, "Direct correlation of transition metal impurities and minority carrier recombination in multicrystalline silicon", Applied Physics Letters **72**, 3482 (1998).

[8] S. A. McHugo, A. C. Thompson, A. Mohammed, G. Lamble, I. Perichaud, S. Martinuzzi, M. Werner, M. Rinio, W. Koch, H. U. Hoefs and C. Haessler, "Nanometer-scale metal precipitates in multicrystalline silicon solar cells", Journal of Applied Physics **89**, 4282 (2001).

[9] A. Bentzen, A. Holt, R. Kopecek, G. Stokkan, J. S. Christensen and B. G. Svensson, "Gettering of transition metal impurities during phosphorus emitter diffusion in multicrystalline silicon solar cell processing", Journal of Applied Physics **99**, 093509 (2006).

[10] T. Buonassisi, A. A. Istratov, M. Heuer, M. A. Marcus, R. Jonczyk, J. Isenberg, B. Lai, Z. Cai, S. Heald, W. Warta, R. Schindler, G. Willeke and E. R. Weber, "Synchrotron-based invetigations of the nature and impact of iron contamination in multicrystalline silicon solar cells", Journal of Applied Physics **97**, 074901 (2005).

[11] K. Graff, *Metal Impurities in Silicon-Device Fabrication,* Springer-Verlag, Berlin, 2000.

[12] G. Zoth and W. Bergholz, "A fast, preparation-free method to detect iron in silicon", Journal of Applied Physics **67**, 6764 (1990).

[13] D. Macdonald and L. J. Geerligs, "Recombination activity of iron and other transition metal point defects in n- and p-type crystalline silicon", Applied Physics Letters **85**, 4061 (2004).

[14] D. Macdonald, P. Rosenits and P. N. K. Deenapanray, "Recombination activity of manganese in p- and n-type crystalline silicon", Semiconductor Science and Technology **22**, 163 (2007).

[15] I. Périchaud and S. Martinuzzi, "Additivity of phosphorus gettering and hydrogenation in multicrystalline silicon cells", in Proceedings 22nd IEEE Photovoltaic Specialists Conference, 877 (Las Vegas, USA, 1991).

[16] L. L. Kazmerski, P. J. Ireland and T. F. Ciszek, "Evidence for the segregation of impurities to grain boundaries in multigrained silicon using Auger electron spectroscopy and secondary ion mass spectroscopy", Applied Physics Letters **36**, 323 (1980).

[17] Y. Tian, Y.-L. Jiang, Y. Chen, F. Lu and B.-Z. Li, "Electrically active defects in Ni-Si silicide studied by deep-level transient spectroscopy", Semiconductor Science and Technology **17**, 83 (2002).

[18] M. Kittler, W. Seifert and K. Knobloch, "Influence of contamination on the electrical activity of crystal defects in silicon", Microeletronic Engineering **66**, 281 (2003).

[19] D. Karg, G. Pensl, M. Schulz, C. Hässler and W. Koch, "Oxygen-realted defect centers in solar-grade, multicrystalline silicon. A reservoir of lifetime killers", Physica Status Solidi (b) **222**, 379 (2000).

[20] O. Klettke, D. Karg, G. Pensl, M. Schulz, G. Hahn and T. Lauinger, "Formation of the chromium-boron complex in solar-grade multicrystalline silicon", in Proceedings 12th International Photovoltaic Science and Engineering Conference, 617 (Jeju, Korea, 2001).

[21] S. H. Park and D. K. Schroder, "Deep-level impurities in edge-defined film-fed-growth silicon", Journal of Applied Physics **78**, 801 (1995).

[22] L. Jastrzebski, L. Lagowski, W. Henley, D. Schielein, S. G. Balster and D. K. Schroder, "Study of Fe and Cr pairing with B in polycrystalline silicon: a possible relation to low resistivity quality degradation", in Proceedings 12th European Photovoltaic Solar Energy Conference, 52 (Amsterdam, The Netherlands, 1994).

[23] J. Lu, M. Wagener, G. Rozgonyi, J. Rand and R. Jonczyk, "Effects of grain boundary on impurity gettering and oxygen precipitation in polycrystalline sheet silicon", Journal of Applied Physics **94**, 140 (2003).

[24] K. Mishra, "Identification of Cr in *p*-type silicon using the minority carrier lifetime measurement by the surface photovoltage method", Applied Physics Letters **68**, 3281 (1996).

[25] K. Bothe, R. Sinton and J. Schmidt, "Fundamental boron-oxygen-related carrier lifetime limit in mono- and multicrystalline silicon", Progress in Photovoltaics: Research and Applications **13**, 287 (2005).

[26] O. Palais, S. Martinuzzi and J. J. Simon, "Minority carrier lifetime and metallic-impurity mapping in silicon wafers", Materials Science in Semiconductor Processing **4**, 27 (2001).

[27] T. Trupke, R. A. Bardos, M. C. Schubert and W. Warta, "Photoluminescence imaging of silicon wafers", Applied Physics Letters **89**, 044107 (2006).

[28] J. Schmidt, "Temperature- and injection-dependent lifetime spectroscopy for the characterization of defect centers in semiconductors", Applied Physics Letters **82**, 2178 (2003).

[29] W. Seifert, M. Kittler and J. Vanhellemont, "EBIC study of recombination activity of oxygen precipitation related defects in Si", Materials Science and Engineering B **42**, 260 (1996).

[30] E. Simoen, C. Claeys, R. Loo, D. DeGryse, P. Clauws, R. Job, A. G. Ulyashin and W. Fahrner, "Characterisation of oxygen and oxygen-related defects in highly- and lowly-doped silicon", Materials Science and Engineering B **102**, 207 (2003).

[31] L. J. Geerligs, "mc-Si: relation between ingot quality and cell efficiency", in Proceedings 12th Workshop on Crystalline Silicon Solar Cell Materials and Processes, 280 (Breckenridge, CO, 2002).

[32] M. Porrini, I. Crössman, M. G. Pretto, R. Scala and R. Wolf, "Improved measurement of carbon in poly- and Cz crystal silicon by means of low temperature FTIR", Solid State Phenomena **108-109**, 591 (2005).

[33] N. Inoue and M. Nakatsu, "Infrared absorption measurement of carbon concentration down to $1\text{x}10^{14}/\text{cm}^3$ in Cz silicon", Solid State Phenomena **108-109**, 621 (2005).

[34] N. Inoue, M. Nakatsu, K. Tanahashi, H. Yamada-Kaneta, H. Ono, V. D. Akhmetov, O. Lysytskiy and H. Richter, "Annealing behavior of new nitrogen infrared absorption peaks in CZ silicon", Solid State Phenomena **108-109**, 609 (2005).

[35] L. J. Geerligs, D. Macdonald and G. Coletti, "Possible reduction of recombination lifetime due to compensated dopants", in 17th NREL Workshop on Crystalline Silicon Solar Cells & Modules: Materials and Processes, (Vail, Colorado, 2007).