

Metallic Impurities in Mono and Multi-crystalline Silicon and Their Gettering by Phosphorus Diffusion

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The concentrations of 42 metal impurities in mono-crystalline microelectronic grade (EG), mono-crystalline solar cell grade (SOG) and cast multi-crystalline SOG silicon have been measured by ICP-MS. In mono-crystalline EG material, all 42 elements were found to be below the detection limit. In mono and multi SOG material we could measure Al, Ti, Cr, Mn, Fe, Ni, Co, Cu, Ga, Mo and Sn. No significant difference was observed between the metal content of the top, middle and bottom of cast multi-crystalline Si (mc-Si). In contrast, a significant difference was observed in top, middle and bottom of solar grade mono-crystalline Si. The outer part of cast multi-crystalline silicon contains higher metal impurities than the center part, likely caused by impurities from crucibles. In cast wafers, phosphorus diffusion gettering (PDG) at 900 °C leads to complete gettering of Cu and Ni. Fe can be partially removed after (PDG) at 900 °C, but it can be effectively removed by ramp-down annealing to 700 °C. In some cast material PDG could reduce metal impurities significantly without a strong improvement of lifetime. Depth profiling of metal impurities in PDG areas shows no detection of Cr contamination because it evaporates during PDG annealing. Also Fe is found to evaporate to some extent.

Introduction

Metal impurities are of significant interest in EG and SOG silicon, since they exhibit fast diffusion in Si and are known to detrimentally impact on minority carrier lifetimes and gate oxide integrity and reduce conversion efficiencies of solar cell materials (1-2). Because of the very high purity of EG silicon, metal impurities in such materials are below the detection limit of almost all instruments. Generally, metal impurity concentrations in SOG silicon materials are several orders of magnitudes higher than respective concentrations in EG silicon materials. Unfortunately, there are very few reports on the metal content of SOG silicon materials. In this study, by employing a combination of several analytical tools including secondary ionization mass spectroscopy (SIMS), laser microwave

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photo-conductance decay (micro-PCD) and inductively coupled plasma mass spectrometry (ICP-MS) metal impurities have been measured in mono-crystalline silicon EG and SOG materials and in multi-crystalline cast SOG silicon wafers for solar cell application.

ICP-MS is a powerful and high performance quantitative elemental analysis tool for measurement of wide ranges of metal impurities in silicon materials. Here we performed ICP-MS analysis of 42 elements and their distribution in many samples of cast type multi-crystalline solar cell silicon from several vendors. We found that the major metal impurities in cast solar grade multi-crystalline (mc) silicon are Al, Fe, Ni and Cu with concentration ranges of 10^{12} to 10^{15} atoms/cm³, medium levels metal impurities are Ti, Cr, Mn and Co ranging from 10^{10} to 10^{13} atoms/cm³, and minor metal impurities are Ga, Mo and Sn with concentration range of less than 10^{10} up to 10^{12} atoms/cm³. Alkali and Alkaline earth elements such as Li, Na, Mg, K and Ca were less than 1×10^{11} atoms/cm³ and the other measured elements Be, Sc, V, Zn, Rb, Sr, Y, Zr, Nb, Pd, Ag, Cd, In, Ba, La, Hf, Ta, W, Ir, Pt, Au, Tl, Pb, Bi, Th, and U were found in concentrations less than 1×10^{10} atoms/cm³.

Fortunately, the negative impact of most of those major, medium and minor metal impurities measured in solar cell grade silicon can be reduced by phosphorus diffusion gettering (PDG) (3-5). An effective method for achieving such gettering of metallic impurities is phosphorus diffusion at higher temperature and post annealing at lower temperature (3,5). Post annealing is applied to allow impurity diffusion and make better use of impurity segregation. Since PDG is segregation-type gettering, the concentration enhancement of impurities in phosphorus-diffused layers is increasing with lowering the temperature of post annealing. In this study we report quantitative data of such effects for Si materials with different amounts of crystal defects in the wafer bulk and different levels of boron concentration, and we discuss PDG versus other types of gettering.

Until now it was reported that iron is the most abundant metallic impurity in mc-Si solar cell materials (6). However, the results of this study demonstrate that Cu and Ni contamination in cast mc-Si can be present at higher concentrations than Fe. The bulk of literature is representing the study of Fe contamination using lifetime measurement (3-4, 7-9). Generally, lifetime measurement technique is a valuable technique to understand recombination activity and to measure concentration of Fe in mono-crystalline silicon. However, in cast mc-Si, because of the presence of many defects and grain boundaries, lifetime is not a reliable technique to understand precisely the Fe concentration level. Therefore, using this technique alone mislead us to understand the capability of phosphorus diffusion gettering, too.

Up to now little has been known about the real concentration level of Ni and Cu in mc-Si because of the lack of techniques with appropriate sensitivity that can determine these metal impurities in mc-Si precisely. In the past, neutron activation analysis (NAA) and secondary-ion-mass spectrometry (SIMS) has been used to

measure Ni and Cu in mc-Si, but they failed to give quantitative and precise information because of the lack of sensitivity (6,10).

Now, with the development of room-temperature acid vapor decomposition method (RT-AVPD) of silicon and the determination of metal impurities with ICP-MS one can measure almost all elements with the highest sensitivity and good precision. This technique has been successfully applied to evaluate metal impurities in the bulk of silicon in the past (11-12). ICP-MS data do not provide direct information regarding the chemical state of metal impurities in silicon. But the low detection limits and precise measurement capability of this technique give strong hints for understanding the chemical state of metals indirectly. For the case of Fe we have double-checked the PDG efficiency at EG mono-crystalline Si and cast SOG multi-crystalline Si using carrier lifetime measurement before and after PDG. The results support our conclusion that, in mono-crystalline and multi-crystalline silicon with high densities of bulk defects including dislocations, the vast majority of Fe cannot be strongly bound to those bulk defects since Fe could be easily and completely removed from the bulk by PDG.

Experimental

Mono-crystalline microelectronic grade silicon wafers with thickness of 725 μm were chosen from differently boron-doped 200 mm CZ-Si crystals. Three kinds of p-type wafers were used, p-, p+ and p++ wafers with boron concentration of 1.3×10^{15} , 5.39×10^{18} and 1.13×10^{19} atoms/ cm^3 , respectively. The concentration of oxygen was in the range $(1.0 - 1.6) \times 10^{18}$ atoms/ cm^3 (old ASTM). For the preparation of highest BMD densities of $>10^6$ defects/ cm^2 , three-step anneal was conducted. Solar grade mono-crystalline CZ-Si with oxygen concentration of $(1.4 - 1.6) \times 10^{18}$ atoms/ cm^3 (old ASTM) from top, middle and bottom parts was used for introducing defined metal impurity levels. The cast multi-crystalline silicon was standard industrial 15 cm x 15 cm material with a resistivity close to 1 Ωcm . The 200 μm thick wafers were from top, middle and bottom parts of ingots with different levels of bulk defects and metal impurities. The mono-crystalline microelectronic samples were cleaned in SC1 and SC2 solutions and subsequently contaminated at levels of 3.5×10^{11} , 3.5×10^{12} and 1.7×10^{13} atoms/ cm^2 for Fe, respectively, and 1.7×10^{13} atoms/ cm^2 for Ti, Cr, Mn, Co, Ni, Cu and Mo using the spin coating method. Before applying PDG the samples were annealed at 1100 $^{\circ}\text{C}$ for 1 hour in N_2 atmosphere to diffuse the metal impurities into the bulk. The Fe concentrations measured in the bulk after annealing were 4.4×10^{12} , 4.6×10^{13} and 2.1×10^{14} atoms/ cm^3 , respectively. The Ti, Cr, Mn, Co, Ni, Cu and Mo concentrations measured in the bulk after annealing were 2.3×10^{12} , 2×10^{13} , 7×10^{12} , 2×10^{14} , 1.9×10^{14} , 2.1×10^{14} and 4.6×10^{11} atoms/ cm^3 , respectively. The cast SOG mc-Si wafers used for PDG was as-received samples with natural contamination levels.

Gettering studies were performed at 900 °C for 90 min. The post-annealing was performed for 2 hours applying ramp down to 800 °C or 700 °C after phosphorus diffusion at 900 °C for 90 min. In order to analyze the metal impurities in the bulk of the wafers and to evaluate segregation coefficients of the different PDG processes, the phosphorus diffusion layers were removed by additional chemical etching, removing 15 µm from each side of the wafers. Before or after PDG, ICP-MS was performed for the measurement of metal impurities in the bulk of respective wafers. The samples were decomposed at room temperature with an acid vapor phase in a closed box containing a mixture of concentrated acids HF/HNO₃/H₂SO₄ (11-12). The instrument detection limits (IDL) for 42 elements measured in this study, using 3 g.- sample for microelectronic grade mono-crystalline silicon and 1 g.- sample used for solar grade mc-Si, are shown in Table 1. After PDG, also depth profiles of the metal impurities near the surface were measured using the drop sandwich etching (DSE) (12-13).

After PDG, the minority carrier lifetime was measured after removing additional

Table 1. Instrument detection limits of 42 elements by ICP-MS using 3g and 1g sample wafer. In this study 3g samples are used for mono and 1g sample is used for mc-Si

No.	Element	IDL (3g sample) atoms/cm ³	IDL (1g sample) atoms/cm ³	No.	Element	IDL (3g sample) atoms/cm ³	IDL (1g sample) atoms/cm ³
1	Li	5.5E+08	1.7E+09	22	Nb	1.6E+09	4.8E+09
2	Be	8.2E+09	2.5E+10	23	Mo	2.2E+09	6.6E+09
3	Na	2.0E+09	6.0E+09	24	Pd	2.0E+09	6.0E+09
4	Mg	1.9E+09	5.7E+09	25	Ag	2.6E+09	7.8E+09
5	Al	1.7E+10	5.1E+10	26	Cd	2.6E+09	7.8E+09
6	K	1.8E+10	5.4E+10	27	In	1.8E+09	5.4E+09
7	Ca	1.9E+10	5.7E+10	28	Sn	3.9E+09	1.2E+10
8	Ti	7.3E+09	2.2E+10	29	Cs	6.0E+08	1.8E+09
9	V	5.6E+09	1.7E+10	30	Ba	1.7E+09	5.1E+09
10	Cr	1.0E+10	3.0E+10	31	La	4.6E+08	1.4E+09
11	Mn	1.1E+09	3.3E+09	32	Hf	3.6E+08	1.1E+09
12	Fe	2.8E+09	8.4E+09	33	Ta	4.4E+08	1.3E+09
13	Co	5.5E+09	1.7E+10	34	W	7.2E+08	2.2E+09
14	Ni	2.6E+09	7.8E+09	35	Ir	4.6E+08	1.4E+09
15	Cu	3.3E+09	9.9E+09	36	Pt	2.2E+09	6.6E+09
16	Zn	6.1E+09	1.8E+10	37	Au	5.8E+10	1.7E+11
17	Ga	2.2E+09	6.6E+09	38	Tl	9.0E+08	2.7E+09
18	Rb	3.7E+09	1.1E+10	39	Pb	2.0E+09	6.0E+09
19	Sr	1.6E+09	4.8E+09	40	Bi	3.9E+08	1.2E+09
20	Y	1.3E+09	3.9E+09	41	Th	2.0E+08	6.0E+08
21	Zr	2.3E+09	6.9E+09	42	U	1.7E+08	5.1E+08

15 µm per side by etching. For reliable measurements of bulk lifetime, the phosphosilicate glass layer on the surface enabled surface passivation. However, removal of phosphosilicate glass layer and metal impurities near the surface and subsequent surface passivation by iodine methanol caused higher minority carrier lifetime. Moreover, with SIMS we measured the P diffusion profiles and metal impurities profiles in the P diffusion layer.

Results and Discussion

Table 2 shows metal concentration levels in the top, middle and bottom of three different crystal types. As can be seen the measured metal impurities concentrations

along the length of the cast mc-Si show no significant difference between top, middle and bottom. In solar grade mono-crystalline Si the results show that all impurities increase more than an order of magnitude along the length from top to bottom. The difference between multi and mono material is an indication of different methods of the crystallization. In cast mc-Si a higher amount of Cr, Mn, Fe, Co, Ni and Cu metal

Table 2. Metal concentration levels in the top, middle and bottom of three different types of crystal.

Element atoms/cm ³	Solar grade multi-crystal silicon			Solar grade mono crystal silicon			Microelectronic silicon		
	Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom
Al	8.0E+12	5.5E+12	6.8E+12	3.9E+15	7.2E+15	1.7E+16	<1.0E+11	<1.0E+11	<1.0E+11
Cr	8.8E+11	3.8E+11	1.7E+11	1.9E+11	2.8E+11	8.1E+11	<1.0E+10	<1.0E+10	<1.0E+10
Mn	4.5E+11	3.5E+11	1.9E+11	4.9E+11	8.4E+11	3.7E+12	<1.0E+10	<1.0E+10	<1.0E+10
Fe	7.8E+12	3.5E+12	3.0E+12	7.7E+13	1.4E+14	5.2E+14	<1.0E+10	<1.0E+10	<1.0E+10
Co	1.3E+11	1.7E+11	1.4E+11	1.0E+10	1.0E+10	1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10
Ni	1.1E+14	7.3E+13	3.4E+13	1.3E+12	2.4E+12	1.4E+13	<1.0E+10	<1.0E+10	<1.0E+10
Cu	3.4E+14	4.6E+14	5.4E+14	2.1E+13	3.8E+13	3.2E+14	<1.0E+10	<1.0E+10	<1.0E+10
Zn	3.2E+10	7.6E+10	1.9E+10	1.0E+10	1.0E+10	1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10
Ti	3.6E+12	3.4E+12	3.7E+12	1.1E+12	2.3E+12	5.8E+12	<1.0E+11	<1.0E+11	<1.0E+11
Ga	3.0E+10	5.3E+10	4.7E+10	2.0E+12	3.8E+12	1.1E+13	<1.0E+10	<1.0E+10	<1.0E+10
Mo	1.9E+10	1.3E+11	1.4E+10	1.0E+10	1.0E+10	1.6E+11	<1.0E+10	<1.0E+10	<1.0E+10
Sn	5.4E+11	7.8E+11	6.9E+11	2.3E+13	3.4E+13	1.1E+14	<1.0E+10	<1.0E+10	<1.0E+10
Be, Li, Na, V, Mg, K, Ca	<1.0E+11	<1.0E+11	<1.0E+11	<1.0E+11	<1.0E+11	<1.0E+11	<1.0E+11	<1.0E+11	<1.0E+11
Rb, Sr, Cs, Ba, Y	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10
Zr, Nb, Pd, Ag, Cd	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10
In, La, Hf	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10
Ta, W, Ir	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10
Pt, Au, Tl	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10
Pb, Bi, Th, U	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10

Table 3. ICP-MS measured metal concentration levels in center and edge area of the same wafer of three cast mc-Si vendors.

Element atoms/cm ³	Vender A		Vender B		Vender C	
	Center	Edge	Center	Edge	Center	Edge
Al	2.9E+13	3.9E+13	6.9E+12	2.2E+12	2.8E+13	2.1E+13
Cr	1.8E+11	7.4E+11	3.8E+11	1.2E+12	4.7E+11	4.2E+12
Mn	1.2E+11	6.1E+12	2.0E+11	8.6E+12	1.6E+11	6.8E+12
Fe	1.7E+12	3.3E+13	3.2E+12	1.3E+14	5.3E+12	1.7E+13
Co	2.9E+10	7.8E+11	1.1E+11	1.8E+12	3.8E+10	7.6E+11
Ni	6.5E+12	1.5E+13	9.2E+13	3.4E+14	3.2E+13	9.3E+13
Cu	6.0E+14	3.0E+15	6.7E+14	6.5E+15	1.2E+14	7.3E+14
Zn	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10
Ti	3.2E+12	3.1E+12	1.9E+12	2.2E+12	4.6E+12	4.3E+12
Ga	2.1E+11	2.3E+11	3.1E+11	3.6E+11	8.6E+10	7.1E+10
Mo	1.7E+10	1.3E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10
Sn	3.1E+10	3.2E+10	4.7E+10	4.8E+10	1.8E+11	1.3E+11
Be, Li, Na, V, Mg, K, Ca	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10
Rb, Sr, Cs, Ba, Y	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10
Zr, Nb, Pd, Ag, Cd	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10
In, La, Hf	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10
Ta, W, Ir	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10
Pt, Au, Tl	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10
Pb, Bi, Th, U	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10	<1.0E+10

impurities has been observed near the edge area as compared to center areas of the same wafer. This is likely caused by the evaporation of interstitially diffusing metal impurities from crucible. No significant difference between edge and center area has been seen for very slow diffusion elements such as Ti, and Mo and substitutional diffusing elements like Sn and Al. Table 3 shows our ICP-MS measurement results of

metal impurities in several vendors of mc-Si for solar cell applications. The result shows a significant amount of Cu and Ni contaminations, which are higher than Fe that is normally regarded as the most abundant element in these materials (6). Among the 42 elements measured by ICP-MS, Cu, Ni and Fe turn out to be the most significant elements in multi-crystalline SOG Silicon.

Figure 1 shows SIMS profiles of Fe, Ni, Cu and phosphorus in p- wafer after PDG at 900 °C and 90 minutes diffusion time. The result shows that the metal impurities are only gettered into the high-concentration region of the in-diffused P layer. Depth profiles of metal impurities on the surface and in the bulk near to the phosphorus diffusion layer were also measured applying ICP-MS after chemically etching the silicon in steps of 0.1, 0.5 and 1 μm by DSE. Figure 2 shows depth profiles of Cr, Fe, Ni, Cu and P using this method. We observed no Cr contamination on the surface and near to the surface in phosphorus diffused layers. Because of the presence of oxygen and chlorine in the phosphorus diffusion annealing ambient, Cr was lost by evaporation during the phosphorus diffusion. Fe is gettered on the surface and very close to the surface region with the highest P concentration, next to the phosphosilicate glass layer. As a result, Fe will be partially removed by evaporation during the POCl_3 process. In contrast, Cu and Ni were not found on the surface of the wafer in the phosphosilicate glass layer. They were completely gettered in the phosphorus diffusion layer, without any loss by evaporation. The bulk concentration of Cu and Ni samples, measured by ICP-MS after RT-VPD, revealed that Ni and Cu are completely gettered by PDG. No detectable traces of Ni and Cu could be found in the bulk of mono-crystalline silicon wafers, for p-, p+, p++ with and without bulk micro-defect (BMD) and cast multi-crystalline silicon with different levels of dislocations as reported in our previous study (5).

Figure 3 shows the concentration of various contamination elements in the bulk of mono-crystalline silicon before and after phosphorus diffusion at 900 °C for 90 minutes and after post annealing to 700 °C for 2 hours as measured by ICP-MS. From these results we can conclude that Cr, Mn, Co, Ni and Cu can be easily gettered at phosphorus diffusion temperature at 900 °C after 90 minutes diffusion time. Fe also could be gettered completely after phosphorus diffusion at 900 °C for 90 minutes and after post annealing to 700 °C for 2 hours. However, Ti and Mo are very slow diffusion elements and cannot be gettered after 900 °C diffusion time and post annealing to 700 °C. In another study of phosphorus gettering of Fe in mono-crystalline silicon, differently boron-doped wafers with and without BMD have been used for investigating the impact of different post annealing (Fig. 4). In differently boron-doped wafers the segregation coefficients are increasing with time of post annealing at 700 °C. Less reduction of total Fe in the bulk is found for high concentration of boron in the mono-crystalline silicon. A possible explanation for the observed effect of high boron concentration on lowering of the segregation coefficient

is a competing path for iron, the well-known electrostatic interaction between Fe^+ and B^- leading to FeB pairs. This competing path for Fe becomes more pronounced at lower temperatures.

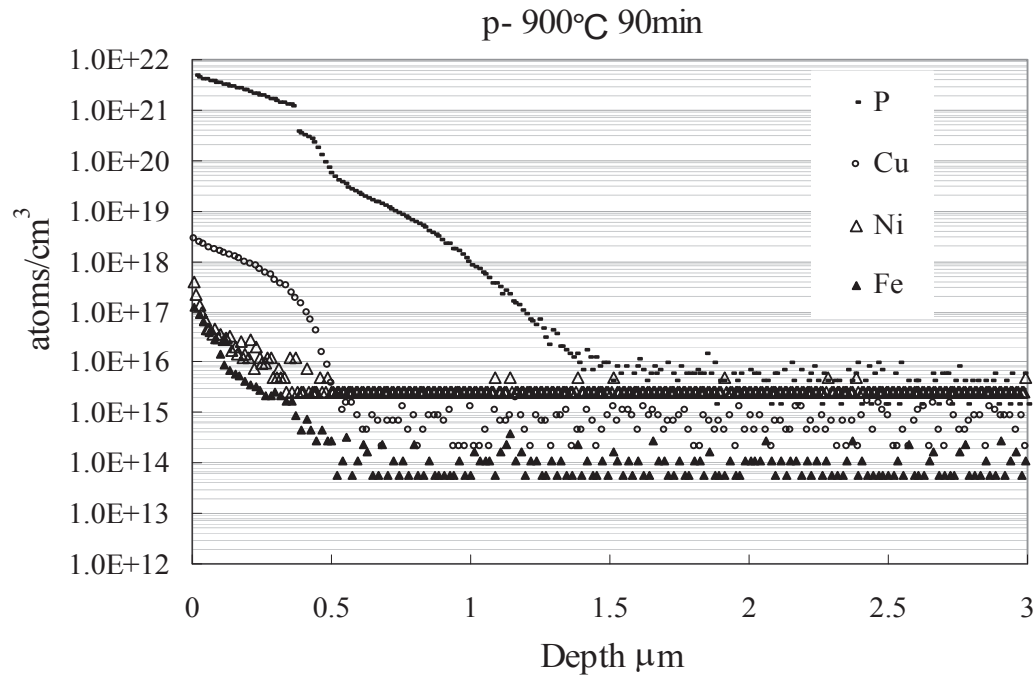


Fig. 1 SIMS profile of Fe, Ni, Cu and P in CZ p- wafer at 900°C and 90 minutes diffusion time.

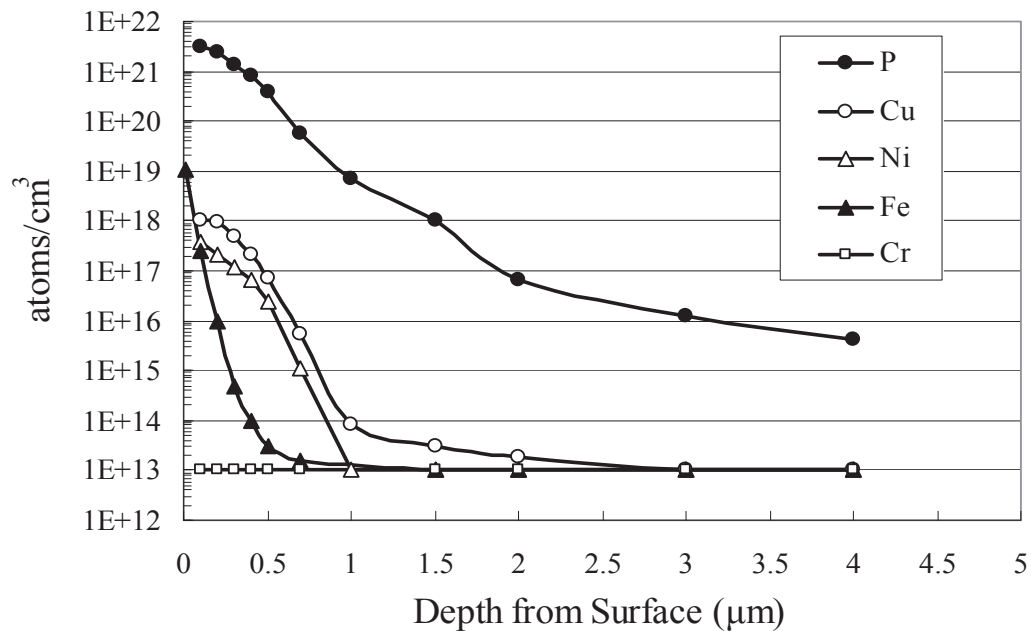


Fig.2 DSE chemical etching depth profile of Cr, Fe, Ni, Cu and P in CZ p- wafer at 900°C and 90 minutes diffusion time.

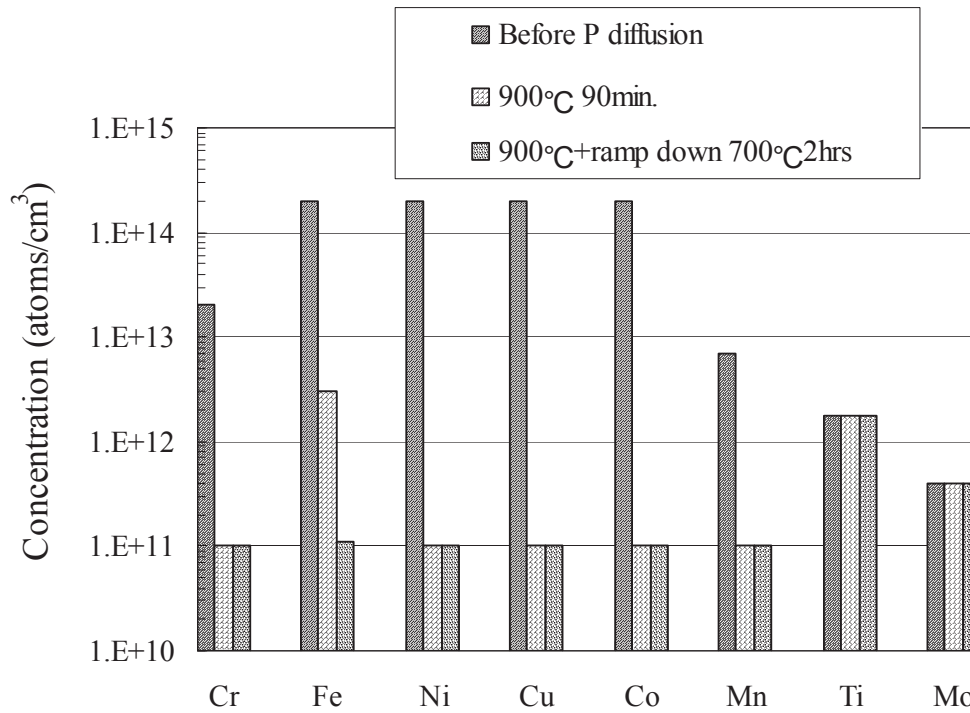


Fig.3 Concentration of various contamination elements in mono-crystalline silicon before and after phosphorus gettering as measured by ICP-MS.

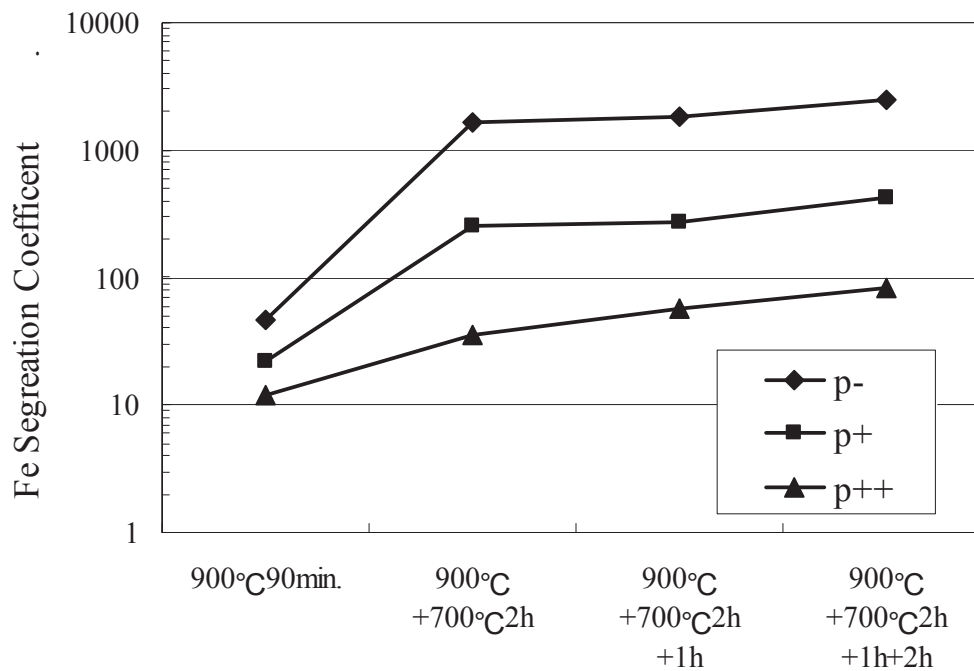


Fig. 4 Segregation coefficient of Fe after 90 minutes phosphorus diffusion at 900°C for differently boron-doped wafers.

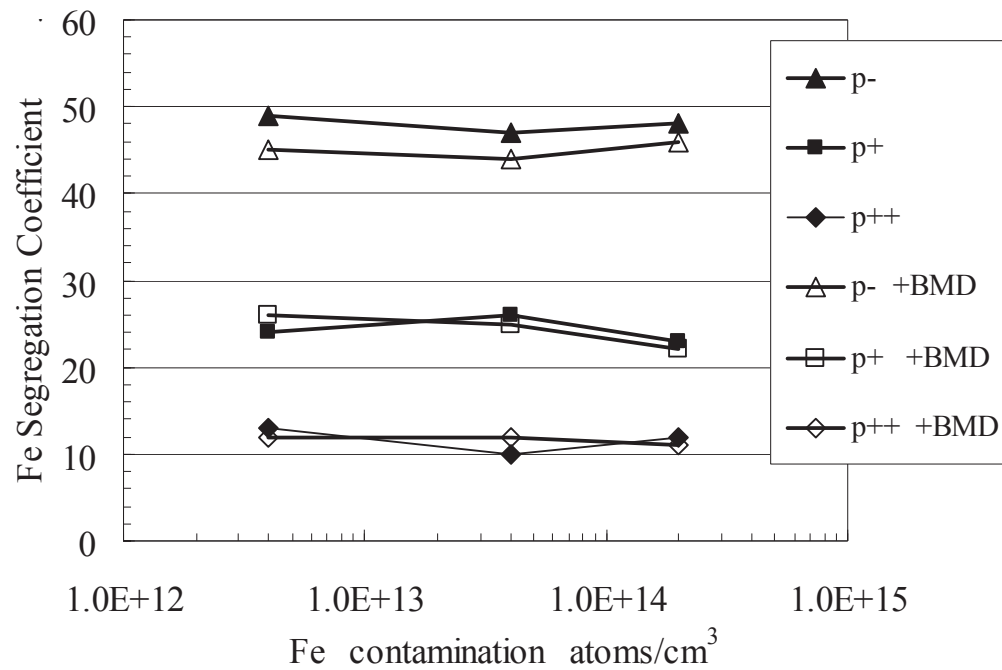


Fig. 5 Segregation coefficient of Fe at 90 minutes diffusion at 900°C for differently boron-doped wafers as a function of Fe concentration.

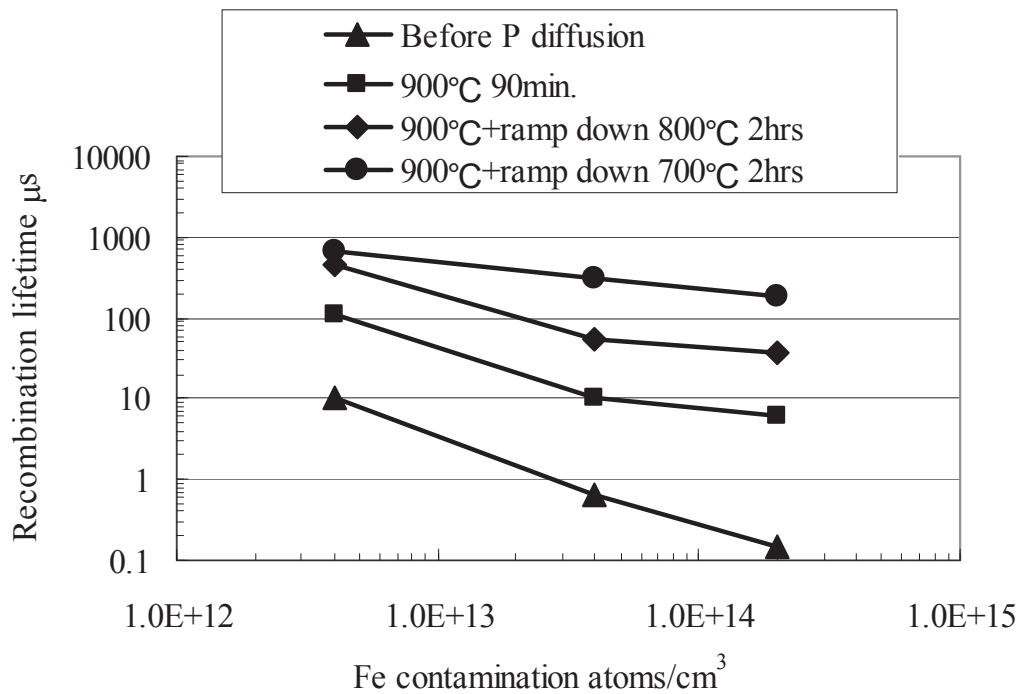


Fig. 6 Recombination lifetime versus Fe concentration before and after phosphorus diffusion and post ramp down annealing.

Figure 5 shows measured segregation coefficients as a function of Fe concentration for 90 minutes 900 °C PDG. Several samples with different concentrations of boron and BMD levels have been used here. For all types of samples studied we do not observe an impact of Fe concentration on segregation coefficients. From this observation we conclude that the solubility of Fe in silicon does not have any impact on gettering efficiency of PDG. The segregation coefficient depends only on the “capture capability” of PDG. The concentration and penetration depth of phosphorus controls this capability and related segregation coefficients. In other words, for Fe basically the temperature and time of phosphorus diffusion are controlling the segregation coefficient. In this study the following formula is used for the calculation of segregation coefficients (SC).

$$SC = \frac{C_{\text{initial}}}{C_{\text{getter}}} \quad (1)$$

C_{initial} is the concentration of Fe in bulk silicon before PDG and C_{getter} is the concentration of Fe in bulk silicon after PDG.

Table 4. Concentration of Fe in p- wafer before and after phosphorus diffusion gettering.

Fe concentration before gettering	900°C 90min.	unit:atoms/cm ³	
		900°C 90min. + 800°C 2hrs (Ramp-down)	900°C 90min. + 700°C 2hrs (Ramp-down)
4.2E+12	<1.0E+11	<1.0E+11	<1.0E+11
4.6E+13	1.5E+12	2.9E+11	<1.0E+11
2.1E+14	3.9E+12	7.3E+11	1.1E+11

To investigate the gettering efficiency of PDG for Fe, the minority carrier lifetimes were measured in different samples of mono-crystalline CZ and mc-Si before and after removal of phosphorus layers. We used the μ -PCD tool WT-85XA of Semilab. 15 μm were removed from both sides of the wafers, and then the surfaces were passivated before lifetime measurement. Fig. 6 and Table 5 show the lifetime results and bulk Fe for different concentrations of Fe before and after PDG. For all Fe concentrations the lifetime increased after PDG. After the ramp down post annealing to 800 °C and 700 °C the lifetime increased further. For wafers contaminated with 2×10^{14} Fe atoms/cm³, the average lifetimes increased 1260 times from 0.15 μs to 189 μs after 2 hours ramp down anneal to 700 °C. Thus, longer post annealing times and lower temperatures are generally more efficient for gettering and related lifetime improvement.

Table 5 shows lifetime measurement results for two different qualities of cast solar-grade mc-Si before and after phosphorus diffusion at 900 °C for 90 min and ramp down post annealing to 700 °C for 2 hours. We see that the lifetime increased

after PDG for all samples. However, for lower-grade or “bad” wafers the lifetimes did not increase to more than 28.8 μs even though the metal impurities were significantly removed by PDG.

Table 5. Minority carrier lifetimes before and after phosphorus diffusion gettering.
unit: μs

Multicrystalline Solar-Grade	Before PDG	900°C 90min. PDG	900°C 90min. + 700°C 2hrs (Ramp-down)
Good	16.0	56.9	76.0
Bad	10.7	18.8	28.8

After lifetime measurement of above wafers the bulk metal impurities of these different grades of mc-Si were measured by ICP-MS and showed 3-5 orders of magnitude reduction after 900 °C for 90 min and 2 hours ramp down post annealing. In fact, after two hours ramp down post annealing all kinds of impurities were under the detection limits of ICP-MS measurement, which is $<10^{11}$ atoms/cm³ in this study. The low lifetimes for mc-Si are not related to the metal impurities because almost all of the impurities had been removed by PDG. Consequently, low lifetime may be controlled by very high density of dislocations and other bulk defects. Additionally, lifetime might be also impacted by lower resistivity of the solar-grade mc-Si (14).

In another study, the lifetime was measured for mono-crystalline p-type wafers with different bulk contamination levels. Figure 7 shows the recombination lifetime versus Fe concentration for 10 Ωcm p-type wafers. A linear lifetime decrease with increasing bulk Fe contamination is obtained. At the bulk Fe concentration of $1\text{E}11$ atoms/cm³, a lifetime of almost 200 μs could be measured.

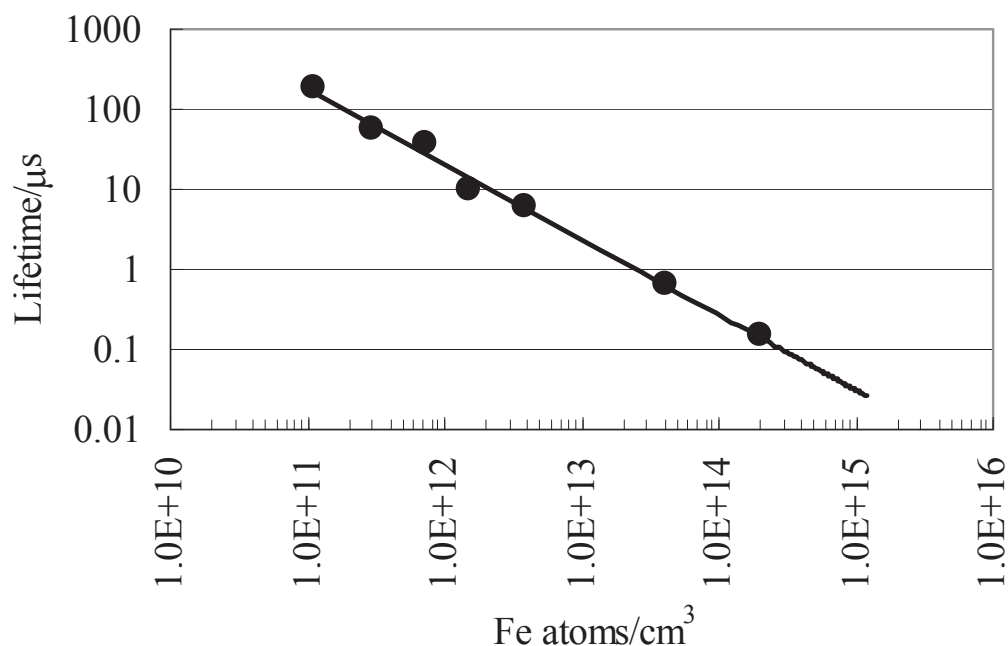
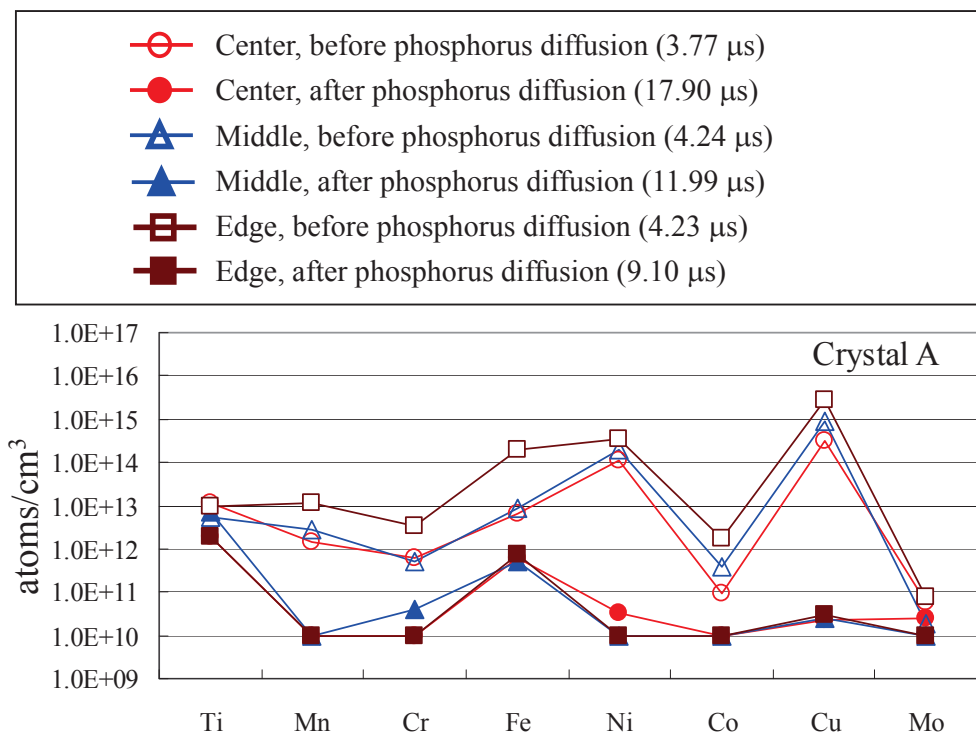
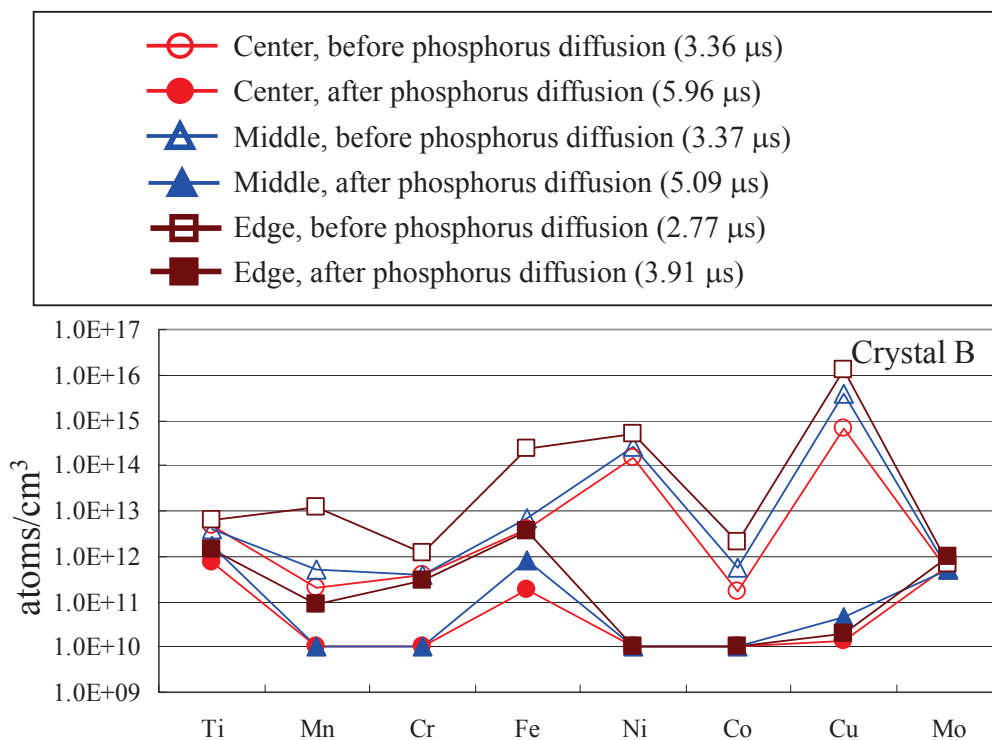


Fig. 7 Recombination lifetime versus Fe concentration for 10 Ωcm p-type wafers.



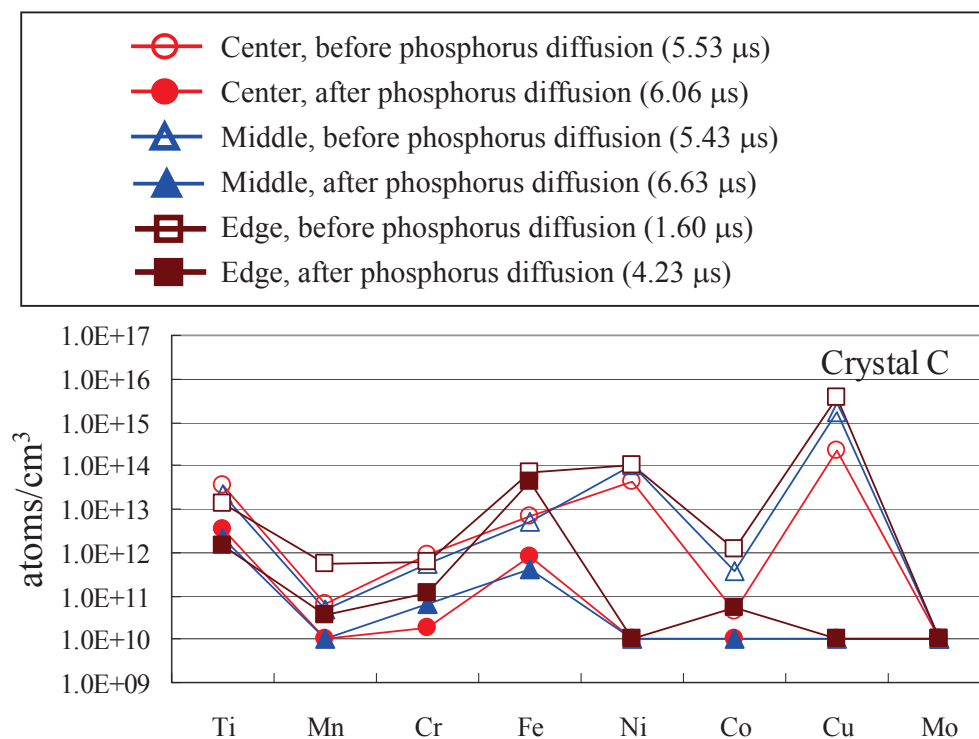


Fig. 8 Concentration of various contamination elements in three cast solar grade mc-Si crystals A, B, C. Different areas of respective wafers before PDG and after PDG are compared and corresponding lifetime results are shown in parenthesis.

Figure 8 shows concentrations of various contamination elements in three cast solar grade mc-Si crystals A, B, C. Different areas of respective wafers before PDG and after PDG are compared and corresponding lifetime results are shown in parenthesis. In all crystals the edge areas are found to have higher contamination levels of Cr, Mn, Fe, Co, Ni and Cu, as compared to center areas of these wafers. No difference between edge and center areas can be seen for the very slowly diffusing elements Ti and Mo and for substitutionally diffusing elements like Al, Ga and Sn. The high concentration of metal contamination in edge areas is probably caused by evaporation of metal impurities from crucibles during the crystal growth, followed by diffusion of those metals during the cooling process of the crystallization. Especially for Fe contamination the edge areas have more than 2 orders of magnitude higher Fe contamination levels. Despite high concentrations of metal impurities in edge areas versus low concentrations in center areas, lifetime results show little differences between these areas. Some of the wafers investigated stem likely from an edge brick where different solidification/cooling conditions can lead to different crystalline structure in edge versus center regions of related wafers. Under such conditions we typically see smaller grains in edge regions, as compared to center regions. After PDG, the contamination level in edge and center regions is found to be either very similar

(crystal A in Fig. 8) or we see remaining higher concentrations in edge regions for Fe (crystals B, C in Fig. 8). Those differences could be related with a different crystal structure in different mc-Si wafers, impacting the precipitation of Fe at crystal growth and partial dissolution of those Fe precipitates during PDG anneal.

Conclusions

Our ICP-MS measurement results of metal impurities in mc-Si for solar cell applications have shown significant amounts of Cu and Ni contamination, partially higher than Fe, which is normally regarded as the most abundant metal impurity in such materials. In cast mc-Si we could not detect a significant variation of the metal content along the crystal length, whereas for mono-crystalline Si we found an increase of more than an order of magnitude towards the end of crystals for all metal impurities detected. The difference between multi and mono material is an indication of different methods of the crystallization. In cast mc-Si, higher amounts of Cr, Mn, Fe, Co, Ni and Cu have been observed near to edge areas as compared to center areas of respective wafers. This can be explained as crucible related contamination by relatively fast, interstitially diffusing metals during crystallization, since we did not see significant edge/center variations for slow diffusers such as Ti and Mo as well as substitutionally diffusing metals like Sn and Al.

In order to reach good PDG effectiveness, expressed as high PDG segregation coefficient, a high near-surface concentration of phosphorus and a relatively low temperature of post annealing are important requisite factors. Slowly diffusing elements like Ti and Mo were not removed by PDG. In the other hand, Co, Ni and Cu impurities, known to be typically associated with dislocations and other bulk defects in as grown mc-Si, are released rapidly from those structural defects and gettered completely at PDG even without using post annealing, indicating no apparent energy barrier. By applying PDG at 900 °C and ramp down anneal to 700 °C for 2 hours also a significant reduction of Fe can be achieved. In mono-crystalline Si heavily contaminated with Fe, the lifetime has been improved more than three orders of magnitude after such ramp down anneal. However, in mc-Si the lifetime did not improve accordingly, most likely due to the large amount of structural defects such as dislocations. Based on bulk lifetime measurements only, until now it is commonly believed that the un-dissolved metal impurities associated with structural defects are responsible for low bulk lifetime. However, our measurements of bulk metal impurities after PDG, revealed very low or no metal contamination. This indicates that the low lifetime in defect-rich mc-Si is not related with the amount of residual metal impurities in the bulk.

We found no impact of BMD concentration levels on the PDG related segregation coefficient. On the other hand, increasing the concentration of boron in

the wafer bulk leads to a strong reduction of the segregation coefficient in the case of iron gettering. Consequently, Fe interaction with boron is clearly stronger than Fe interaction with structural defects in the bulk of silicon wafers. Depth profiling of metal impurities in phosphorus gettering areas shows no detection of Cr and Mn because these elements will evaporate during oxidation and the presence of chlorine in the diffusion ambient. Also Fe can partially evaporate during phosphorus diffusion anneal. Depth profiles of Fe, Ni and Cu in the phosphorus layer reveal that they are present very close to the wafer surface where the highest concentration of phosphorus is located, confirming segregation-type gettering at PDG.

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