IMPACT OF COMMON METALLURGICAL IMPURITIES ON MC-SI SOLAR CELL EFFICIENCY: P-TYPE VERSUS N-TYPE DOPED INGOTS.

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ABSTRACT: Silicon solar cells based on n-type silicon wafers are less sensitive to carrier lifetime degradation due to several common metal impurities than p-base cells. The theoretical and experimental indications for this have recently received considerable attention. This paper compares p-type and n-type cells purposely contaminated with relatively high levels of impurities, processed by industrial techniques. The impurities considered are Al, Ti, and Fe, which are the dominant impurities in metallurgical silicon and natural quartz. The work also preliminary addresses the question whether the optimal wafer resistivity is the same for n-type as for p-type base mc-Si cells.
Keywords: silicon, feedstock, impurities

1 INTRODUCTION

This paper compares p-type and n-type silicon solar cells purposely contaminated with relatively high levels of impurities, processed by industrial techniques. The impurities investigated, Al, Ti and Fe, are important in feedstock production involving quartz and carbon, such as by metallurgical routes, because they are the major impurities in natural quartz. A metallurgical process, i.e., reaction of quartz and carbon, offers a perspective for large scale and low cost production of solar grade silicon.

The work is also relevant for other feedstock production techniques and for ingot casting, because quartz and steel are dominant materials in equipment for feedstock production and ingot growth.

It is known that the interstitial point defects Ti, V, Cr, Mo, Fe in silicon capture electrons much more effectively than holes [1]. Therefore these defects are expected to be less detrimental for carrier recombination lifetime in n-type silicon, where holes are the less abundant (minority) carriers, than in p-type silicon, where electrons are the minority carriers. The same effect applies to the aluminium-related defect observed in Cz wafers [2]. This asymmetry in capture cross sections also causes a different sensitivity to wafer resistivity. Recombination lifetime in n-type wafers due to these defects is practically insensitive to resistivity, while in p-type wafers it can show a strong decrease with decreasing resistivity.

The aim of this work is to determine the optimum doping (type and resistivity) of mc-Si solar cells that contain a non-negligible amount of Ti, Al and/or Fe impurities. The first aim is to determine whether higher concentrations of these impurities can be tolerated better in n-type silicon than in p-type silicon. The second aim is to determine whether for n-base cells a lower resistivity is allowed than is commonly allowed for p-base wafers, thus enhancing the cell V_{oc} and efficiency. This paper presents first results mainly for silicon contaminated with a mix of the impurities.

2 EXPERIMENTAL

2.1 Experimental ingots

Two p-type and two n-type ingots were grown with a mix of impurities. Additional p-type ingots were grown with the individual impurity Al or Ti.

The silicon was crystallised by directional solidification into a 12 kg ingot, wafered, and processed to cells by industrial cell processing (experimental cell processing based on industrial techniques, for the case of n-type base).

The p-type ingots were doped with boron to result in a base resistivity of approx. 1.5 Ωcm. The n-type ingots so far were doped with phosphorous to a much lower base resistivity of around 0.1 Ωcm. N-type ingots without impurities but with low resistivity, as well as with individual impurities and normal resistivity have been made but have not yet been analysed.

Most ingots contained a significant amount of carbon. However, earlier studies [3] showed that this carbon has only a small effect on the cell properties. For the levels of impurities studied here, we neglect the effect of carbon.

Ingot code and impurity concentrations in feedstock are given in Table 1. Note the distinct difference between impurity level in feedstock versus in ingot or wafer. The ppm-levels in feedstock are reduced to ppb or less in the ingot due to segregation.

Table I: List of ingots and concentration of impurities in the feedstock. Impurity levels in ppmw (parts-per-million by weight).

ingot	type	ρ	impurities		
		Ωcm	Al	Ti	Fe
p-5Al	p	1	5		
p-10Ti	p	2		10	
p-10Ti16Fe-A	p	2		10	16
p-10Ti16Fe-B	p	2		10	16
n-5Al1Ti3Fe	n	0.1	5	1	3
n-40Al10Ti70Fe	n	0.2	40±20	10±5	70±30

2.1 Experimental ingots

The p-type cell process was a standard industrial process: alkaline saw-damage etch, phosphorous diffusion in an IR belt furnace, remote plasma-enhanced CVD of a SiNx front surface coating, screen printed metallisation, and co-firing. For the experiments in this abstract, the typical cell efficiency with this process on good quality wafers was 14.5-15.0%.

The n-type cell process was an early version of the cell process developed in the NESSI project [4]. It is mostly based on industrial process steps: alkaline saw-damage etch, boron diffusion in a quartz tube furnace, remote plasma-enhanced CVD of a SiNx front surface coating, screen printed metallisation, and co-firing. For the experiments in this paper, the typical cell efficiency with this process on good quality wafers was 12.5%. One of the aspects limiting the cell efficiency is the absence of surface passivation of the boron emitter by the SiNx coating.

The cell size was typically $(100mm)^2$, in some cases $(125mm)^2$.

As reference for the experimental ingots, conventional mc-Si ingots were used. For the p-type cells, several regular mc-Si ingots were used. For the n-type ingots, reference mc-Si wafers from several experimental n-type ingots were supplied by Deutsche Solar [4].

3 RESULTS

3.1 Experimental ingots

The results on the p-type doped ingots were analysed and published previously [3].

The resistivity profiles of the p-type ingots are relatively flat because boron hardly segregates (k_{eff}~0.8). Only the Al-contaminated p-type ingot shows some more resistivity variation due to doping by Al with segregation coefficient k_{eff}~0.007. The resistivity in the n-type ingots also follows a profile in approximate agreement with Al-segregation. This is consistent with the fact that while phosphorous dominates the type of doping, Al segregation dominates the change of resistivity through the ingot.

In ingots n-5Al1Ti3Fe and n-40Al10Ti70Fe the Al and P-concentrations were measured by chemical analysis. The resistivity is higher by a factor 2 (n-5Al1Ti3Fe) to 3 (n-40Al10Ti70Fe) than expected from the chemical dopant concentration. Most likely this indicates a reduced carrier mobility in these ingots (due to the other impurities).

3.2 Cell results: p-type ingots

Fig. 1 shows typical examples of the I-V parameters and the internal quantum efficiency for some of the p-type ingots. The IQE of one of the ingots (p-10Ti16Fe-B) is suppressed at short wavelengths because of insufficient removal of saw damage (the ingot was sawn with a different sawing technique - ID saw). The suppression of IQE at long wavelengths is due to the metallic contaminants in the experimental ingots. It was analysed more precisely for the individual impurities Ti and Al in a previous paper [3]. The suppression of IQE in p-10Ti and p-10Ti16Fe is similar, and therefore is concluded to be largely due to the Ti present in these ingots, rather than the Fe present additionally in p-10Ti16Fe.

3.3 Cell results: n-type ingots

Fig. 2 shows the I-V parameters and the internal quantum efficiency of n-type ingot n-40Al10Ti70Fe. For the ingot n-5Al1Ti3Fe, the I-V parameters are not directly comparable because of different cell process conditions.

The striking effect that V_{oc} for cells from ingot n-40Al10Ti70Fe is higher than for the reference wafers, was not observed for all cell batches from this ingot, nor for ingot n-5Al1Ti3Fe. The effect appears to depend on process conditions.

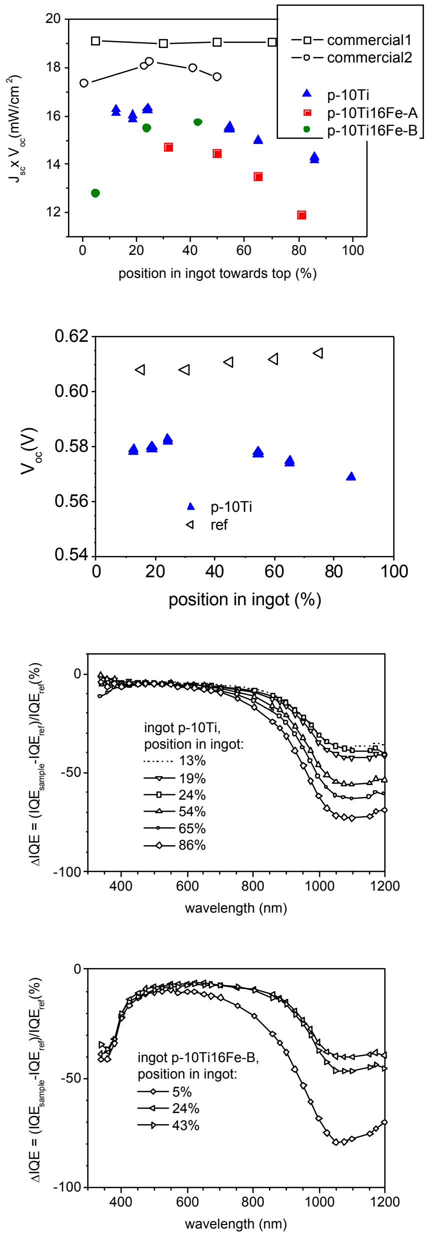

Figure 1: $J_{sc}V_{oc}$ product, V_{oc}, and internal quantum efficiency (the IQE is presented as deviation in % from average of reference ingot "commercial1") for the p-type ingots.

3.4 Cell results: L_D and recombination lifetime

The parameters of major importance in this paper, to characterise the impact of the impurities, are the carrier diffusion length and lifetime, derived from the internal quantum efficiency. These are shown for all investigated ingots in Fig. 3.

4 DISCUSSION

4.1 Internal quantum efficiency and carrier lifetime

The minority carrier diffusion length can be derived from a Basore-fit (1/IQE versus $1/\alpha(\lambda)$)of the infrared part of the internal quantum efficiencies. The impact of impurities on solar cell response is determined by this diffusion length. Since the lifetime is the parameter directly coupled to impurity concentrations, this discussion focuses on the lifetime. A disadvantage of n-type base material which should be kept in mind is that the minority carrier diffusivity in n-type Si is roughly a factor 3 lower than in p-type, for the same resistivities. In Fig. 3 both diffusion length and carrier lifetime are given (the estimated diffusivity was used to calculate the carrier lifetime).

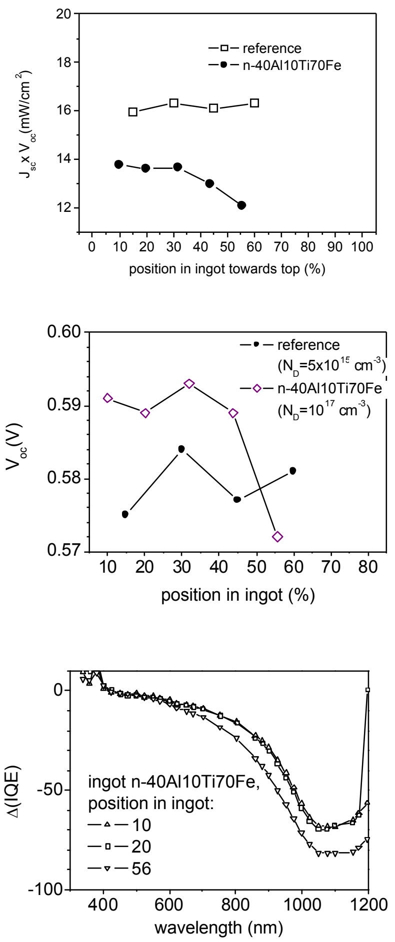

Figure 2: $J_{sc}V_{oc}$ product, V_{oc}, and internal quantum efficiency (the IQE is presented as deviation in % from average of the reference ingot) from n-type ingot n-40Al10Ti70Fe.

According to the Scheil equation,

$$C_S = k_{eff} C_0 (1 - f_s)^{k_{eff}-1},$$

the concentration of an impurity as a function of position x in the ingot (x=0..1, from bottom to top) should be given by:

$$N_t \propto \frac{1}{1-x}, \text{ and therefore } \frac{1}{\tau} \propto N_t \propto \frac{1}{1-x}.$$

This behaviour is visible in Fig. 3.

Ingots n-5Al1Ti3Fe and p-5Al are both doped with approx. 5 ppmw of Al but ingot n-5Al1Ti3Fe has approx. 10-30x lower resistivity than ingot p-5Al. Nevertheless, ingot n-5Al1Ti3Fe has significantly higher lifetime than ingot p-5Al. Thus, Al is much less harmful for the recombination lifetime in the n-type ingot. However, due to the lower diffusivity of minority carriers in the n-type silicon, the difference in *diffusion length* in these two ingots is rather small.

Ingot n-40Al10Ti70Fe is doped with an amount of Ti comparable to the p-type ingot p-10Ti, and additionally has a large amount of Al and Fe, and a resistivity approx. 10x lower than the p-type ingots. Nevertheless, the carrier lifetime is similar to the p-type ingots with 10 ppmw of Ti, and only a factor 3 lower than ingot n-5Al1Ti3Fe. Due to the different minority carrier diffusivities, the *diffusion length* in ingot n-40Al10Ti70Fe is smaller than in the p-type ingots doped with 10 ppmw of Ti.

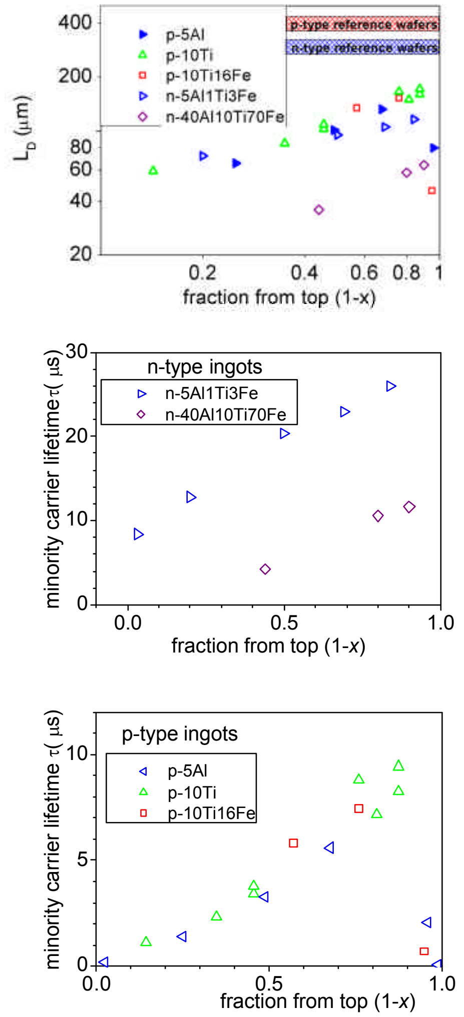

Figure 3: Minority carrier diffusion length (determined from the internal quantum efficiency) and corresponding minority carrier lifetime. For the conversion from diffusion length to lifetime, the additional suppression of carrier diffusion in the n-type ingots by a factor 2-3 was taken into account.

4.2 Ingot resistivity and V_{oc}

An advantage of low resistivity n-type wafers can be that it increases the open circuit voltage of the cell. Normally (in p-type cells with common impurities such as Fe) a low resistivity causes a decrease of carrier lifetime. Therefore the potential gain in V_{oc} is offset by lifetime-related losses, especially of J_{sc}. A typical optimal resistivity is 1 Ωcm.

In n-type silicon, according to our (preliminary) results, the low resistivity is less harmful for minority carrier lifetime, and the low resistivity may be used to some advantage. As shown in Fig. 2 the V_{oc} of the contaminated but highly doped wafers from ingot n-40Al10Ti70Fe is even better than the V_{oc} of the uncontaminated but normally doped reference wafers. This is probably why the $J_{sc}V_{oc}$ product of cells from ingot n-40Al10Ti70Fe, relative to the reference cells, is high, similar to that of the p-type ingots doped with 10 ppmw Ti, despite the lower diffusion length.

However, as mentioned in section 3.3, this remarkable effect in V_{oc} was not always observed and appears to depend on cell process conditions.

4 SUMMARY

The effects of contaminants in p-type and n-type doped multicrystalline silicon wafers were compared experimentally. The reduction of cell efficiency due to contamination of silicon feedstock with titanium, iron and aluminum was analysed. We observed favorable effects due to the n-type doping. The studied metal impurities have lower impact on carrier lifetime in the n-type doped wafers than in the p-type doped wafers. The situation with respect to carrier diffusion length is less clear.

The low n-type base resistivity (~0.1 Ωcm) leads, despite high metal impurity content, in some cases to higher open circuit voltages than the reference n-type cells with ~1 Ωcm base resistivity. Thus, the combination of low n-type resistivity and high impurity content performs better than expected.

So far, n-type ingots were investigated in which are present, simultaneously, high impurity concentrations as well as high doping levels. The effect of resistivity and the effects of individual impurities will be studied separately. This will allow to model and quantify the impact of the impurities in an n-base solar cell, so that it can be compared directly with our previous results for a p-type base. Such a more accurate analysis should also show whether the advantages for carrier lifetime observed in this paper are larger than the disadvantage of the lower diffusivity in n-type silicon.

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