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HIGH EFFICIENCY N-TYPE MULTICRYSTALLINE SOLAR CELLS

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ABSTRACT

Research and development activities on silicon solar cells mainly focus on cost reduction and performance optimisation. An alternative technology with a large potential regarding cost reduction and improvement of environmental footprint is n-type multicrystalline silicon solar cell technology. N-type multicrystalline silicon shows several advantages compared to p-type multicrystalline silicon. One of them is the lower sensitivity to some metallurgical impurities which is an important feature when solar cells are produced from less pure silicon feedstock. In general, high minority charge carrier lifetime and competitive diffusion length have been reported for n-type mc-Si.

This paper presents a brief overview of the n-type multicrystalline silicon material properties exposed in the literature, together with the behaviour of n-type multicrystalline material at the solar cell level. Fabrication processes for high efficiency n-type multicrystalline solar cells based on industrial techniques are presented.

INTRODUCTION

Today, the majority of solar cell production is based on p-type multicrystalline silicon (mc-Si) wafers using a very mature technology. However, many alternative solar cell technologies, based on wafers or thin films, are under investigation. The overall objective of these investigations is to develop a lower cost (cost/Wp) technology, with possibly also lower use of materials and improved environmental footprint. N-type mc-Si solar cells, the subject of this paper, represent an alternative technology which can potentially fulfil this objective, with only modest changes to the current wafer and cell production processes.

One of the advantages of n-type solar cells is that they can make use of alternative silicon feedstock sources. Due to the exponential increase of the cell production, the feedstock supply rapidly evolved into a shortage, which may continue in the years to come. Therefore, n-type silicon is of interest because approximately 2000 tonnes/year of n-type wastes of Czochralski (Cz) grown Si monocrystals are available and a large part of it, eventually after mixing with lightly doped silicon, may be used in production of n-type mc-Si ingots by means of directional solidification. Also, upgraded metallurgical silicon may be more conveniently used for production of n-type cells, in situations where n-type dopants are present and hard to remove (compensated p-type ingots will normally have reduced yield due to type change in the ingot; n-type ingots do not suffer from this disadvantage). Additionally, we will show in this paper that some metallurgical impurities have lower impact in n-type ingots. The same is true for the boron-oxygen defect.

Research and developments on solar cells based on n-type Si substrates and low-cost screen-printed processing became active in the last 4-5 years, and several cell structures, such as boron-diffused emitter type, and the aluminium alloy emitter have been reported. Several groups have reported very high pre- and post processing minority carrier recombination lifetimes in n-type mc-Si wafers, low recombination activity of transition impurities (Fe for example) or very high carrier diffusion lengths. Considering inexpensive commercial-grade silicon wafers and high throughput industrial processes inducing a wide variety of impurities and defects, the question concerning the type of silicon, suitable for high efficiency solar cells, has to be considered: p-type or n-type.

The objective of this paper is to highlight the properties of the n-type mc-Si material (electronic properties and solar cell processes), and show that it is an excellent base material for high efficiency commercial solar cells using cost effective processes.

WHY CHOOSING N-TYPE MATERIAL AS A BASE MATERIAL?

• High minority carrier lifetime and diffusion length

One fundamental reason for the requirement of high minority carrier lifetimes in n-type silicon – compared to p-type – is the lower mobility of the holes (for 1 Ωcm Si: $\mu_p \approx 1/3\mu_n$) which corresponds to a lower diffusion coefficient. That means, for the same diffusion length, the lifetime of the holes needs to be three times higher than the lifetime of electrons in p-type Si. Such higher lifetimes, and even lifetimes exceeding the factor of 3, can be expected for n-type Si because of the absence of lifetime reducing boron oxygen complexes (B-O), and lower recombination activity of transition metal impurities (e.g. Fe).

Cuevas et al [1] demonstrated exceptionally high minority carrier lifetime on n-type mc-Si material from Eurosolare SpA of varying resistivity, even approaching levels of n-type monocrystalline silicon.

The effective minority carrier lifetime measured on mc-Si n-type material after phosphorus (P) gettering exceeds the millisecond lifetime mark. The best result has been reached for a 2.3 Ωcm wafer, whose average lifetime of 1.6 ms corresponds to a hole diffusion length of 1.4 mm. Ref [1] also shows the spectacular consequence of the phosphorus gettering on the trapping effects which are frequently associated with the presence of metallic impurities. The results obtained on a 0.36 Ωcm resistivity wafer show a lifetime increase by a factor of 10 after P gettering. The lifetime also remains practically constant over a broad range of injection levels, which is a very desirable feature for solar cell operation. A similar behaviour is found for the post-gettering lifetime of the 0.9 Ωcm wafer, except at high carrier densities where the lifetime is affected by Auger and emitter region recombination.

Martinuzzi et al [2] measured, on a raw n-type material voluntarily contaminated with Fe, Co and Au (dose of 10^{13} cm^{-2}), a bulk lifetime τ_p of around 100µs. After gettering, they reach, at least, 300µs corresponding to diffusion length values around 200 to 300 µm. Such high lifetime values have never been observed in p-type mc-Si raw wafers, or they have been measured only after long gettering treatments by phosphorus diffusion or aluminium-silicon alloy gettering [3]. In phosphorus gettered samples, the measured values of diffusion length are higher than 500µm. The authors refer to a LBIC contrast scan map indicating values of diffusion length and note that conversely to p-type material, they did not find regions in which there is no improvement of the material and where the diffusion length remains very poor (few tens of µm).

• Gettering effect in n-type mc-Si

Gettering of metal impurities is an essential step in the production of efficient photovoltaic devices from relatively impure materials, such as multicrystalline silicon. Such metals impurities may be present in numerous forms, including substitutional or interstitial ions or in precipitates of oxides, silicates or silicides. Some of the more important metal contaminants are most dangerous when present interstitially, such as Fe and Cr. Gettering techniques are usually very effective at removing interstitial impurities, and since these are often the dominant lifetime-killers, large improvements in lifetime can result.

Macdonald et al. [4] investigated phosphorus gettering effect performing Neutron Activation Analysis (NAA) on mc-Si. Thanks to this measurement technique, phosphorus gettering effect was monitored for various contaminating elements: As, Sb, Sn, Zn (substitutional), Ag, Co, Cr, Cu, and Fe (interstitial). It turns out that phosphorus gettering does not have any effect on substitutional elements. Their inability to be gettered arises because of their much lower diffusivity than interstitial impurities, meaning that gettering deep into the wafer bulk in the relatively short time used is not possible. The three dopant species (As, Sb and Sn) do not introduce deep levels in silicon, and hence they have little impact on carrier lifetimes. The ineffectiveness of gettering then is of little consequence for these elements. While the substitutional diffusers did not respond to gettering, they show that for Ag, Co, Cr, Cu and Fe there is a definite reduction, often quite large. These elements all diffuse interstitially, and hence have much higher diffusivity.

Other gettering techniques have been implemented on n-type mc-Si materials. J.Libal et al. [5] focused their study on characterisation and material improvement in terms of charge carrier lifetimes by various gettering techniques and by H-passivation. The n-type multicrystalline material casted by Deutsche Solar shows high initial carrier-lifetimes of >100 µs (only the saw-damage has been removed). The effective lifetime of the studied material is significantly improved by gettering or H-passivation. Aluminium gettering proved to be the most effective gettering process (τ_{eff} = 220 µs). Phosphorus gettering improve the lifetime is in the same order of magnitude (τ_{eff} = 204µs) and was increased to 218µs by an additional H-passivation step.

• Impurities sensitivity

N-type mc-Si demonstrates resilience to contamination introduced during processing or wafer formation. This is because for many interstitial metallic impurities commonly found in silicon solar cells, the impurity capture cross section for holes is much less than the capture cross section for electrons.

Macdonald and Geerligs [6] modelled and measured the impact of the recombination caused by intentional Fe contamination on the low injection lifetime of n-type and p-type wafers. The results clearly show that the n-type wafers are much less strongly affected.

Coletti et al. [7] measured the effect of Fe contamination on the minority carrier lifetime of p-type and n-type ingots after phosphorus gettering, boron/phosphorus co-diffusion and hydrogenation. The as-grown minority carrier lifetime in the iron doped ingots is about 1–2 and 6–20 µs for p and n type, respectively. After gettering and hydrogenation the lifetimes in the n- and p-type Fe doped ingots are approaching each other (lifetime is about two times higher in the n-type than in the p-type ingot). As-grown lifetime values for the n-type reference are similar to the gettered values of the n-type Fe ingot.

Schmidt et al. [8] theoretically determined the recombination parameters of isolated Cr and CrB pairs in phosphorus doped n- and boron-doped p-type silicon wafers. Contrary to Fe, Cr has larger capture cross section for holes and electrons (σ_n=2,3.10^{-13} cm^2 σ_p= 1.10^{-13} cm^2). In consequence, relatively low concentration of interstitial Cr in bulk Si causes large lifetime degradation in both p- and n-type mc-Si.

Ti has a diffusivity several orders of magnitude lower than Cr or Fe. Because of its low diffusivity, titanium, once introduced, remains at interstitial sites within the Si lattice after cooling to room temperature. Interstitial Ti produces mid-gap donor and acceptor levels with large capture cross sections and has a pronounced influence on the lifetime of minority carriers in p- and n-type silicon. However, Geerligs et al. compared effective diffusion length of p- and n- type mc-Si ingots voluntarily contaminated with Ti (fig 1). The measurement results show that the carrier diffusion length of the n-type wafers is not affected, whereas the carrier diffusion length of the p-type samples is.

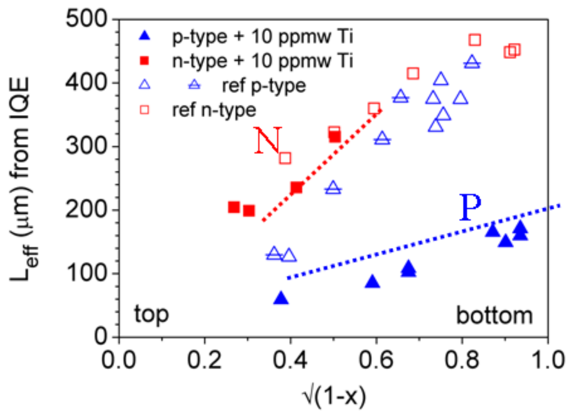

Figure 1 - Comparison of L_{eff}, of n-type and p-type mc-Si ingots contaminated with Ti as a function of ingot position.

• Crystal defects

The recombination rate of minority carriers in a mc-Si wafer is also related to the interaction between impurities and crystal defects. The extended defects themselves are involved in recombination, and in the large grains of mc-Si, dislocations are the most harmful defects when they are decorated by impurities. Since the capture cross sections of the metallic impurities are smaller in n-type silicon, it is expected that the consequences of the impurity-defect interactions are reduced, and this reduction will be enhanced after gettering because of impurity concentration decrease (ref [2]).

Martinuzzi et al. [2] made lifetime and LBIC contrast scan map of high densities extended defects regions. Local values of minority carrier lifetime measured are at least ten times higher than those found in a p-type sample containing similar defect densities. In a region where the dislocation density is about 10^7 cm^{-2} , diffusion length of 120 µm and lifetime of 60µs were measured which confirm the low recombination strength of extended defects.

Cotter et al [9] reported the excellent tolerance of n-type wafers to induced or introduced defects. For feedstock considerations, the defects that exhibit high hole lifetime and low electron lifetime suggest that n-type silicon wafers would be a better choice for high-efficiency commercial silicon solar cells.

Also Woditsch et al, in patent US6576831, describe that crystal defects in n-type silicon are less active than in p-type silicon, and as a consequence, n-type mc-Si with low proportions of active grain borders can be obtained.

In contrast to the previous mentioned paper, Geerligs et al. [10] note a different trend in the recombination activity of impurity point defects between p- and n-type mc-Si. Ref [10] show that the as-grown extended crystal defects degrade less after phosphorus gettering in p-type wafer than in n-type wafer. After hydrogenation, the lifetime improvement is similar for both p-type and n-type which means no large difference in tolerance to extended defects between both types.

In conclusion, high minority carrier lifetimes and competitive diffusion length have been reported in multicrystalline n-type material. In addition, n-type mc-Si demonstrated resilience to common contaminations during process or wafer formation thanks to a lower capture cross section for holes than for electrons, for many impurities. Reduction of recombination activity after gettering in n-type mc-Si has been shown to be as good as in p-type material. Crystallographic defects commonly introduced during wafer growth, such as grain boundaries or dislocations, may exhibit low recombination strength in n-type mc-Si, but literature reports about this vary.

All these features combined with an appropriate fabrication process would lead to high efficiency silicon solar cells based on n-type mc-Si substrates.

This raises the question of why only p-type mc-Si wafers are used for solar cell production. The main reasons for this are somewhat historical and have their origins over 40 years ago in the early days of commercial silicon solar cell production when space power applications dominated the commercial market. In this context, controlled irradiation studies showed significant degradation of the minority carrier lifetime and junction characteristics for n-type wafers [11]. Other reasons for the p-type domination on the solar cell market are related to fabrication process issues such as easier emitter formation by phosphorus diffusion.

However, the degradation under high-energy radiation argument is not adequate in the context of high-efficiency solar cells for terrestrial applications. Moreover, new processes achieve excellent boron emitter formation and passivation and n-type solar cells benefit from structure design advantages such as open rear side metallisation, suitable for thin wafers and enhancing internal reflection.

N-TYPE PERFORMANCES AT THE CELL LEVEL

• Gettering efficiency of p-type emitter versus n-type emitter

Gettering via standard phosphorus diffusions remove easily a selection of interstitial impurities (e.g. Fe) but the possible effect of these impurities on the recombination rate in the diffused regions where they eventually reside has to be considered. Macdonald et al. [12] investigated whether realistic concentrations of Fe gettered to both boron- and phosphorus-diffused regions can cause a measurable increase in recombination in those regions, as characterized by the emitter saturation current density J_{oe}. The author established that the gettering efficiency of the phosphorus diffusions is much greater than for boron diffusions, despite the fact that a greater number of boron atoms are required to achieve the same sheet resistance, due to lower carrier mobility. The extracted J_{oe} values show that even though more than 99% of the Fe is present in the phosphorus diffused regions and glass, there is no measurable impact on the J_{oe} values. However, there is a clear two- to three-fold increase in the saturation current for boron diffused samples. These observations can be explained by the large difference in capture cross sections for electrons and holes for the likely forms of Fe in these samples, as mentioned earlier. Since the diffused regions are always in low injection, the recombination rate through the Fe-related centres will be determined by the minority carrier capture cross section. In the n-type phosphorus diffusions, the Fe is likely to be in interstitial form, and the corresponding cross section (for holes) is very small, around 7.10^{-17} cm^2. For p-type diffused regions, the minority carrier capture cross section is much larger (at least 2.10^{-15} cm^2). This means the impact of the Fe would be at least a factor of 20 greater in the p-type diffusions. In other words, for n-type multicrystalline bases, which are of increasing interest, iron gettered to boron-diffused emitters may still have a significant impact on recombination.

• Experimental results

▪ *Fe contamination*

G. Coletti et al. [7] investigated the impact of Fe on n- and p-type wafers sliced from directionally solidified microcrystalline ingots and on performance of solar cells fabricated from these wafers. Short circuit current (Jsc) times open circuit voltage (Voc) product is reported as a function of vertical position in the ingot for the p- and n-type references and for the Fe contaminated ingots. The performance is remarkably close to the reference at positions between about 60% and 70% of the ingot height for the p-type ingots. In the n-type ingot, the addition of Fe reduces the solar cell performance in most of the ingot. Jsc×Voc is reduced in the bottom and the middle. In the top, the performance of the n-type reference decreases, approaching the value of n-type Fe contaminated ingot. The authors showed that the main reason for the degradation is a reduction in the diffusion length. From spectral response and reflectivity measurements, the internal quantum efficiency (IQE) and the effective average minority carrier diffusion length (L_{eff}) were calculated. The main differences between the references and Fe doped ingots are in the long wavelength response. No increase in recombination in the emitter region is visible in the IQE measurements differently than reported by Macdonald et al. [10]. However, Mihailetchi et al. [13] note, for the same Fe-contaminated cells, a more distinct drop in Voc than for non-Fe-contaminated cells, and attribute this to recombination in the emitter, in line with the findings of Macdonald. Further experimental work is needed in order to discriminate between the possible causes.

The authors also described a difference in the crystal structure development for both the Fe doped ingots compared to the reference ingots. At the bottom and at the top of the Fe doped ingots the density of the crystal defects is enhanced, both in comparison to about 70% height within the same ingots and in comparison to the reference ingots. This is reflected in the solar cell efficiencies, which are reduced in the bottom and top, but are comparable to the reference at around 70% height. The increasing defect concentration in the top of the Fe doped ingots may be related to the increasing iron concentration in the melt. In the bottom, the initial high concentration of Fe in the silicon melt may have originated a transient nucleation and growth disturbance during the early solidification phase. However, these effects may be particular for the very heavy contamination (50 ppmw) introduced in these experiments.

▪ *Solar cell efficiency variation in n-type mc-Si ingots – effect of base resistivity*

Mihailetchi et al. [13] experimentally investigated the correlation between resistivity and solar cell efficiency on n-type mc-Si wafers. Two multicrystalline n-type ingots grown in the same furnace have been selected for this investigation: a compensated ingot (called ingot 5) which is partially p-type (boron dominates over antimony) and partially n-type (antimony dominates over boron) doped. Solar cells have been fabricated on 156.25 cm^2 wafers distributed to cover a resistivity range of 0.8 to 7.7 Ωcm from the first ingot and 0.3 to 2.2 Ωcm from the second ingot. The measured JscxVoc product increases with resistivity for cells made from ingot 6 while it stays rather constant for cells of ingot 5 for resistivity larger than 1.3 Ωcm. These results suggest that the optimum base resistivity for n-type multicrystalline Si feedstock lies between 1.5 to 4 Ωcm. However, recent results in our group for an ingot of higher resistivity (described in the next paragraphs), indicate that this result is probably dependent on ingot growth conditions, and not universally valid.

From lifetime data resulting from fitting internal quantum efficiency data (IQE), in ref. [13] it is observed that a resistivity higher than approximately 1.3 Ωcm is required in order to ensure that bulk diffusion length is higher than the average wafer thickness for both ingots. The lifetime as a function of resistivity also shows, for low resistivity, a linear dependence, suggesting activity of some impurity which is relatively harmful in n-type base (e. g. Au, Zn, perhaps Cr).

A similar study on n-type mc-Si wafers from the Dai-Ichi Kiden company has been also carried out in our group. The results show an increase of efficiency with resistivity, even up to a resistivity higher than 7 Ωcm. The JocxVoc trend is actually similar to the trend described by Mihailetchi et al. [13] but shifted to higher resistivity. The reason for the difference in efficiency variation as a function of the resistivity is still under investigation, and could be due to different defects in the various ingots.

- **ECN process for n-type solar cell**

The n-type mc-Si material characteristics described in the previous sections offer perspective for fabrication of high efficiency commercial solar cells. The main challenge resides in the designing of an adapted fabrication process. One of the major development areas of the n-type mc-Si solar cell process remains the passivation of the front side boron emitter. Since the conventional way to passivate phosphorus emitters for the p-type solar cell process, using a PECVD-SiNx layer, results in a poor or no passivation for boron emitters, a new way of passivating boron doped surfaces needs to be developed. Mihailetchi et al. [13] have developed a new method to passivate boron emitters which brought new potential to the n-type multicrysatlline silicon industrial solar cell process. This new method relies on the same PECVD SiNx technology, as is widely used in industry to passivate phosphorus emitters, and is industrially applicable with no substantial increase in cost or process time.

This method employs an ultrathin silicon oxide between the emitter and the SiNx. An almost 6-fold enhancement in the lifetime and 60 mV higher implied Voc is observed for lifetime test devices after firing. These values outperform even the results obtained using thermal SiO_2/PECVD SiNx stacked layers as a passivation method. Since the method employs a low-temperature oxidation process, possible deterioration of, e.g., the base material, is minimized.

Our simplified cell process protocol is illustrated in figure 2 and a structure of the fabricated n-type cells is presented in figure 3. The rear-side metallization has an open structure that can enhance the internal reflection, as well as increase the annual energy yield by employing bifacial modules. The cell process led to efficiencies of 16.7% on multicrystalline and 18.5% on monocrystalline wafers of 125mm size (independently confirmed by ISE CalLab) [14]

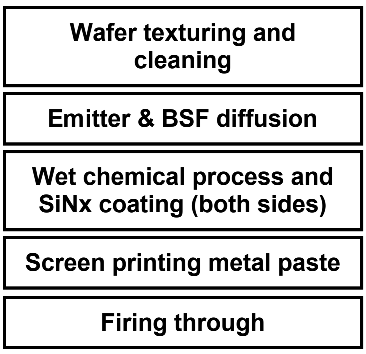

Figure 2 - Major process steps for making industrial screen printed n-type solar cells.

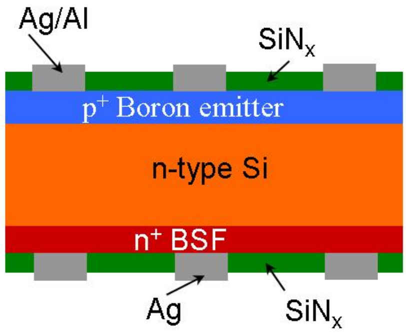

Figure 3 - Schematic cross-section of the n-type solar cell.

In the context of the European FOXY project, modules were made of n-type mc-Si solar cells - made from Deutsche Solar wafers by ECN using the process described above – and were assembled and tested by Isofotón. After 3 months of outdoor exposure, no signs of degradation have been observed. Also, on separate (mini-)modules, damp heat and thermal cycling tests were carried out at ECN and have shown a fill factor degradation of less than 2%.

Recently, Naber et al. [14] demonstrated that an alternative wet chemical process for creating the SiO_2 passivation layer facilitates a further enhancement of the Voc by 4 to 5 mV. The Voc has (on Cz of 1 Ωcm) an average value of 634 mV and a peak value of 639 mV.

New passivation methods for boron emitter are under development to utilise the full potential of n-type solar cells. New technology involving negatively charged dielectric layers such as Al_2O_3 are under investigation. Benick et al. [15] have proven the excellent surface passivation of Al_2O_3 deposited by Atomic layer deposition technique (ALD) on cell level based on float zone Si substrates. They reported very high IQE values of ~100% in the 300–600 nm range demonstrating the excellent front surface passivation on B-doped emitters provided by Al_2O_3. Atomic layer deposited Al_2O_3 may therefore also offer excellent passivation for n-type mc-Si wafers.

CONCLUSION

The results presented in this paper confirm that n-type multicrystalline silicon offers a significant opportunity for commercial high-efficiency silicon solar cells. From a feedstock point of view, n-type mc-Si material exhibits an excellent tolerance to a large number of impurities and it has been reported that the effect of interactions between impurities and extended defects can be strongly reduced compared to p-type mc-Si material. In consequence, compared to p-type, n-type mc-Si has high minority carrier lifetime and competitive minority carrier diffusion length suggesting that this n-type mc-Si is better suited for high efficiency commercial silicon solar cells. Simple and cost effective concepts for solar cell manufacturing based on n-type mc-Si wafers are in development and already led to record efficiency of 16.7% on large area multicrystalline wafers. One of the key process steps to reach such high efficiencies is the boron emitter passivation which currently outperforms the best passivation obtained for the conventional n-type emitter on p-type wafers (Joe=23 fA/cm^2 for p-type emitters vs. Joe≈200 fA/cm^2 for n-type emitters).

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