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# N-type multicrystalline silicon wafers and rear junction solar cells

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**Abstract.** *N*-type silicon presents several advantages compared to *p*-type material, among them, the most important is the small capture cross sections of metallic impurities, which are neatly smaller. As a consequence lifetime and also diffusion length of minority carriers should be neatly higher in *n*-type than in *p*-type, for a given impurity concentration. This is of a paramount interest for multicrystalline silicon wafers, in which the impurity-extended crystallographic defects interaction governs the recombination strength of minority carriers. It is experimentally verified that in 1.2  $\Omega$  cm raw wafers lifetimes about 200  $\mu$ s and diffusion lengths around 220  $\mu$ m are measured. These values increase strongly after gettering treatments like phosphorus diffusion or Al-Si alloying. Scan maps reveal that extended defects are poorly active, although in regions where the density of dislocations is higher than  $10^6$   $\text{cm}^{-2}$ . Abrupt  $p^+n$  junctions are obtained by Al-Si alloying after annealing between 850 and 900  $^\circ\text{C}$ , which could be used for rear junction cells. Such cells can be processed by means of similar processing steps used to make conventional *p*-type base cells.

**PACS.** 72.20.Jv Charge carriers: generation, recombination, lifetime and trapping

## 1 Introduction

Today the photovoltaic industry produces *p*-type base solar cells, which the related technology is very mature, however due to the exponential increase of the cell production the feedstock quantity is limited and we have to face a shortage in the years to come. However, *n*-type silicon is also 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 low doped silicon may be used in production of *n*-type multicrystalline ingots (mc-Si) by means of directional solidification. *N*-type material possesses some remarkable advantages. First, there are little or no boron-oxygen complexes and it has been reported that the lifetime of minority carriers does not decrease with the injection level [1]. As a consequence *n*-type base cells should work more efficiently at low illumination levels compared to *p*-type based cells. Secondly, and this is of a paramount importance, the minority carrier capture cross sections of metallic impurities, frequently found in processed silicon, are markedly smaller for holes than for electrons [2]. This property of *n*-type silicon was clearly explained by Macdonald and Geerligs [3] on the basis of the formation of donor trap levels in the gap which are positively charged or neutral, and can be strongly attractive for

electrons or poorly attractive for holes. Interstitial iron which is one of the more harmful contaminant in mc-Si wafers is a good example because the capture cross sections for electrons and for holes, reported by Istratov [4], are  $\sigma_n = 5 \times 10^{-14}$   $\text{cm}^2$  and  $\sigma_p = 7 \times 10^{-17}$   $\text{cm}^2$ , respectively. Assuming that Shockley-Read-Hall (SRH) recombinations occur and that interstitial iron is the dominant impurity, very high lifetime values are expected for holes in *n*-type silicon. Although the diffusion coefficient of electrons is 3 times higher than that of holes, it is expected that diffusion lengths of minority carriers, in such a simple configuration, are neatly higher in *n*-type than in *p*-type silicon (provided the impurity concentration is the same in both types of wafers). The formation of FeB pairs in boron doped silicon, which are less detrimental for electron lifetime [3, 4], reduces but does not cancel the advantage of *n*-type over *p*-type silicon. The same tendency is observed for several other metallic impurities [3], except for chromium, for which the capture cross sections are closed in both *n* and *p* type silicon [5]. Obviously, there are other impurities and different sources of recombination centers, like fast and slow diffusers, precipitates and crystallographic defects in mc-Si wafers, and the reality is more complex. In addition, the capture cross sections of minority carriers determined by deep level transient spectroscopy are not those occurring in the base of a solar cell in which the electric field is negligible and the temperature

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is higher than 300 K (this point will be developed later in this paper).

Today, multicrystalline silicon (mc-Si) wafers or ribbons are the dominant material in photovoltaic industry. Such materials are characterized by the presence of a high density of extended crystallographic defects, like grain boundaries, dislocations and twins, which are more or less associated with segregated impurity atoms. These impurities are metallic fast diffusers (mainly iron, chromium and copper), oxygen atoms or oxygen precipitates and it is the interaction between extended defects and impurities that determines the recombination rate of minority carriers in the wafers. The extended defects, by themselves are little involved in recombinations, 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 fast diffusers are smaller in  $n$ -type silicon, it is expected that the consequences of the impurity-defect interaction are strongly reduced, and this reduction will be enhanced after a gettering treatment because impurity concentrations decrease. However, due to the growth conditions of the mc-Si ingots, i.e. directional solidification of Cz crystal wastes in a mould, oxygen atoms are also present in actual concentrations larger than those deduced from infrared spectroscopy. Indeed such a technique detects only interstitial oxygen atoms while precipitated or aggregated atoms are not taken into account. Oxygen precipitation occurs certainly at dislocation cores, at dislocation clusters and at grain boundaries. These precipitates can, in turn, trap metallic impurities and become recombining, as observed in  $p$ -type silicon. However, their surfaces are expected to have a hole repelling positive charge, and so in  $n$ -type materials such precipitates have been found less harmful for minority carriers [6].

Recently, experimental results have reported exceptional values of lifetime in  $n$ -type wafers cut from ingots or from ribbons: Cuevas et al. [1], Schmiga et al. [7] and Libal et al. [8] have found lifetime values of several hundred of  $\mu$ s in raw materials and values in the range of ms in wafers gettered by a weak phosphorus diffusion.

Such interesting properties can be useful for solar cells and several papers have been published that dealt with the use of monocrystalline  $n$ -type silicon with junctions made by boron or aluminium in-diffusion. The Ebarra group has intensively investigated  $n$ -type monocrystalline silicon ribbon solar cells in which a rear junction was made by means of aluminium-silicon alloying [9, 10]. This technique is very attractive because it is well known that in-diffusion of aluminium in silicon occurs at relatively low temperatures after the formation at 570 °C of the Al-Si eutectic alloy, which behaves like a metal. Indeed, during the cooling down of the structure, the alloy retracts while a few micrometers of silicon remain saturated with aluminium. A  $p^+$ -type layer is formed in the silicon just above the alloy, and if the alloy is annealed at  $T > 700$  °C, the doping level reaches  $10^{19}$  cm<sup>-3</sup>, i.e. the value of the solubility limit of Al in Si at such temperatures. As a consequence an acceptable  $p^+n$  junction could be obtained more eas-

ily than with boron diffusion, possibly with the additional benefit of a gettering effect.

The aim of this paper is to show, by means of scan maps of minority carrier diffusion lengths and lifetimes, that  $n$ -type mc-Si is an excellent material, because the recombination strength of dissolved impurities and extended crystallographic defects is low, neatly smaller than in  $p$ -type mc-Si, and that the Al-Si alloy formation gives rise to acceptable  $p$ - $n$  rear junction solar cells (RJC).

## 2 Experimental

$N$ -type 350  $\mu$ m thick mc-Si wafers were cut from ingots grown at EniTecnologie in a directional solidification furnace, following the usual production conditions for  $p$ -type ingots. The silicon feedstock was composed of top and tail parts of  $n$ -type Cz ingots. The resistivity of the investigated wafers measured by the four point probe technique was 1.2  $\Omega$  cm, and the  $n$ -type conductivity was verified using the hot probe test and also by means of a contactless tester (Semilab P/N tester).

To obtain an evaluation of the ratio  $\sigma_p/\sigma_n$  in the base of a solar cell and to compare its value with that given by DLTS, we have contaminated voluntarily  $p$  and  $n$ -type wafers ( $\sim 1$   $\Omega$  cm) by means of Fe, Co and Au ion implantation at an energy of 100 keV and a dose of  $10^{13}$  cm<sup>-2</sup>. Then the samples are annealed in argon at 850 °C for 2 h, bulk lifetimes  $\tau_n$  and  $\tau_p$  are measured and the ratio  $\sigma_p/\sigma_n$  is evaluated assuming that SRH statistics occurs.

Lifetime and diffusion length ( $L$ ) of minority carriers were determined by means of the microwave contactless phase shift ( $\mu$ WPS) and surface potential voltage techniques, which gave overall values averaged on a few cm<sup>2</sup>. Using a focused infrared monochromatic ( $\lambda = 960$  nm) light spot, the  $\mu$ WPS and the light beam induced current techniques (LBIC) allow scan maps of  $\tau$  and  $L$  to be obtained with a spatial resolution of 50  $\mu$ m. Notice that  $\mu$ WPS technique working at a microwave frequency of 10 GHz and at various modulation frequencies of the near infrared excitation leads to the simultaneous evaluation of the bulk lifetime and of the surface recombination velocity, and does not need surface passivation [11]. The LBIC technique working at various near infra red wavelengths leads to the determination of  $L$ . All these techniques have been described in details, previously, in references [12, 13]. The collecting structures used for the LBIC technique was Au-Si( $n$ )-Si( $n^+$ )-Al. A 8 nm thick semitransparent gold layer was deposited on the  $n$ -type front surface, while the back surface was phosphorus diffused (850 °C–20 min) in order to create a  $n^+$  layer needed to make an ohmic contact.  $N^+np^+$  rear junctions made by means of aluminium-silicon alloying were used to make rear junction solar cells (RJC), which the illuminated front surface was passivated by an  $n^+$  layer due to phosphorus diffusion. The  $p^+n$  junction was obtained after deposition by electron gun evaporation of a 1.2  $\mu$ m thick layer of aluminium and annealing at 850 °C for 10 min. The metallisations of the cells result from the back Al-Si alloy, which is quasi metallic, and

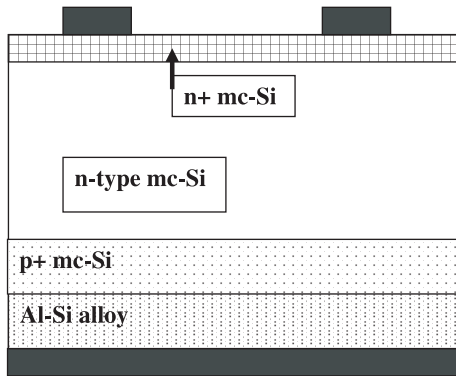


Fig. 1. Structure of a rear junction solar cell.

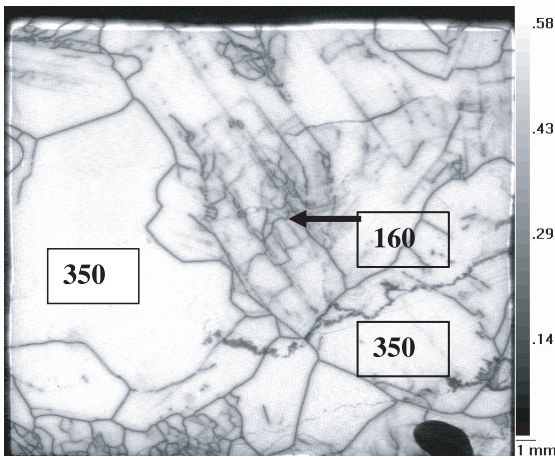


Fig. 2. Typical LBIC contrast scan map at  $\lambda = 980$  nm of a raw sample with local values of minority carrier diffusion length in  $\mu\text{m}$ .

from a front silver grid deposited by vacuum evaporation. The structure of the cell is described in Figure 1. RJC cells were also prepared using a back side screen printed aluminium layer in order to simulate industrial processing steps used to make  $n^+pp^+$  conventional cells.

Chemical etching was used to reveal the presence of extended defects in the investigated samples. Gettering treatments consisted in phosphorus diffusion from  $\text{POCl}_3$  at  $900^\circ\text{C}$  for 1 h.

### 3 Results

In the raw  $n$ -type material the mean values of  $\tau_p$ , averaged in  $25\text{ cm}^2$  wafers, are around  $100\ \mu\text{s}$ . After gettering they reach, at least,  $300\ \mu\text{s}$ , in agreement with Cuevas et al. [1], Schmiga et al. [7] and Libal et al. [8]. The mean diffusion length values are also very high, as  $200$  to  $300\ \mu\text{m}$  are measured in raw wafers. Such high values have never been observed in  $p$ -type mc-Si raw wafers, or they had been measured only after long gettering treatments by phosphorus diffusion, or aluminium–silicon alloy gettering [14].

In phosphorus gettering samples, the values of  $L_p$  are higher than  $500\ \mu\text{m}$ , in agreement with the results of Cuevas et al. [1]. A typical LBIC contrast scan map of

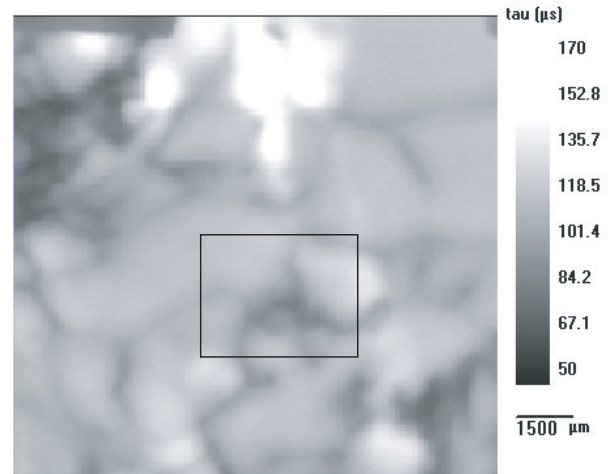


Fig. 3. Lifetime scan map of a sample containing dislocation arrays, grain boundaries and subgrain boundaries. Notice that the lower value is  $60\ \mu\text{s}$  in the central area (demarcated by a rectangle) although the extended defect density is very high.

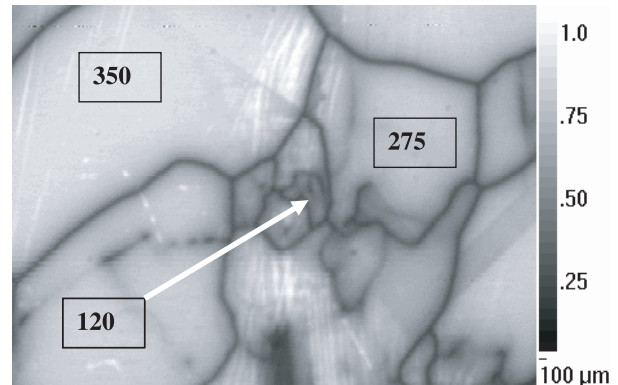


Fig. 4. Scan map of the LBIC contrast of Figure 3 sample at  $980$  nm. (contrast is intensified in order to reveal extended defects). Some values of  $L_p$  are indicated in  $\mu\text{m}$ .

a raw wafer is given by Figure 2 and some local values of  $L_p$  are indicated in  $\mu\text{m}$ . Conversely to  $p$ -type materials, we don't have found regions in which there is no improvement of the material and where the diffusion length remains very poor (few tens of  $\mu\text{m}$ ).

Figures 3 and 4 show the scan maps of lifetime and of LBIC contrast for a sample in which extended defects are present in high densities, as revealed by the microphotography of Figure 5. In the LBIC map some values of  $L_p$  are indicated in  $\mu\text{m}$ .

Notice that the local values of  $\tau_p$  are at least ten times higher than those found in a  $p$ -type sample containing similar defect densities. Table 1 gives the values of lifetime measured in  $n$  and  $p$ -type samples, contaminated under the same conditions, and the deduced values of the capture cross section ratio  $\sigma_n/\sigma_p$ . This ratio is different of that obtained by DLTS [2,3], but it is sufficiently large for Fe, for FeB and for Co in order to confirm the advantage of  $n$ -type silicon and to check that the values given by DLTS are acceptable. Both maps and the



**Fig. 5.** Optical microphotography of the central part of Figure 3 sample after chemical etching. The lower values,  $60 \mu\text{s}$  for  $\tau_p$  and  $180 \mu\text{m}$  for  $L_p$ , are found in regions where the dislocation density is higher than  $10^6 \text{ cm}^{-2}$ .

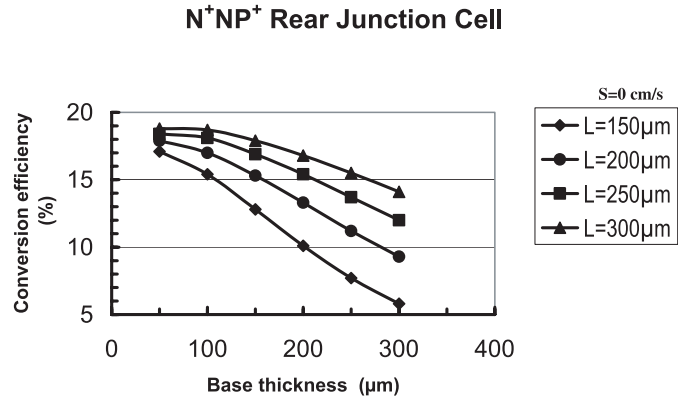
**Table 1.** Values of the ratio of capture cross sections for minority carriers obtained from DLTS and from lifetime measurements at room temperature in  $n$  and  $p$  type mc-Si samples contaminated under the same conditions. In  $p$ -type  $\tau_n$  is measured before and after dissociation of FeB pairs.

| Impurity        | $\sigma$ ( $\text{cm}^2$ )       | $\tau$ ( $\mu\text{s}$ ) | $\sigma_n/\sigma_p$ (DLTS) | $\sigma_n/\sigma_p$ ( $\tau$ ) |
|-----------------|----------------------------------|--------------------------|----------------------------|--------------------------------|
| Fe <sub>i</sub> | $\sigma_n = 5 \times 10^{-14}$   | $\tau_p = 300$           | 700                        | 300                            |
|                 | $\sigma_p = 7 \times 10^{-17}$   | $\tau_n = 1$             |                            |                                |
| FeB             | $\sigma_n = 2 \times 10^{-15}$   | $\tau_n = 20$            | 28                         | 15                             |
| Au <sub>s</sub> | $\sigma_n = 2.2 \times 10^{-15}$ | $\tau_p = 25$            | 18                         | 4                              |
|                 | $\sigma_p = 1.4 \times 10^{-16}$ | $\tau_n = 6$             |                            |                                |

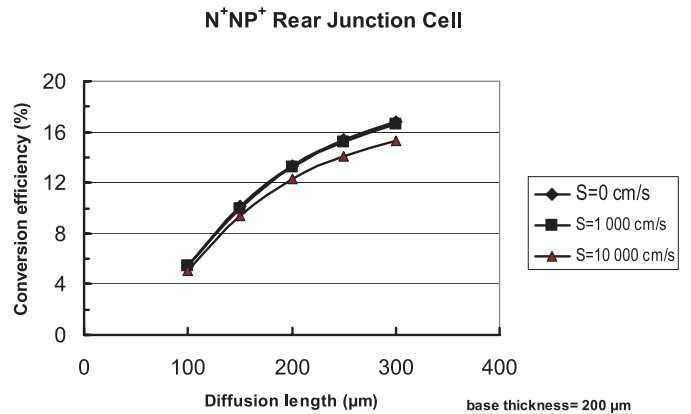
microphotography reveal the same features of recombining defects and their comparison shows that the high values of  $L_p$  are due to the high values of  $\tau_p$ . In a region of the sample of Figure 3, demarcated by a rectangle and in which the dislocation density is about  $10^7 \text{ cm}^{-2}$ , it is found that  $L_p \sim 120 \mu\text{s}$  and  $\tau_p \sim 60 \mu\text{s}$ . Such values confirm that the recombination strength of the extended defects is very low.

With this excellent material we can realize easily junctions for solar cells by Al-Si alloying, as said in the introduction. Because the alloy is electrically conductive but not transparent to sunlight, rear junction cells (RJC) must be used, which work efficiently provided that the minority carrier diffusion length is higher than the substrate thickness and that the front surface is passivated (by means of a slight phosphorus diffusion).

Computed variations of the conversion efficiency as a function of the base thickness for various  $L_p$  values and for a passivated illuminated surface (recombination velocity  $S = 0 \text{ cm/s}$ ) is given by Figure 6. Using thin  $n$ -type multicrystalline silicon wafers, which the thickness is smaller than  $120 \mu\text{m}$ , in which  $L_p$  reaches 2 to 3 times the wafer thickness, the conversion efficiency of the RJC can reach 19%. As the passivation level of the illuminated surface is critical, we have also computed the variation of the conversion efficiency as a function of  $L_p$  for various values of



**Fig. 6.** Conversion efficiency versus base thickness of a RJC for various diffusion length  $L_p$  and surface recombination velocity  $S = 0 \text{ cm/s}$ .



**Fig. 7.** Conversion efficiency of a RJC versus  $L_p$  for various values of  $S$ .

$S$  and a wafer thickness of  $200 \mu\text{m}$ . Figure 7 shows that the conversion efficiency does not change significantly when  $S$  is below  $10^3 \text{ cm/s}$ . We have verified that values of  $S$  lower than  $100 \text{ cm/s}$  are obtained after a front surface phosphorus diffusion at  $850 \text{ }^\circ\text{C}$  for 20 min and that acceptable  $p^+n$  junctions are obtained after annealing of the Al-Si structures at temperatures in the range  $850$  to  $900 \text{ }^\circ\text{C}$ . The diffusion potential is around  $0.8 \text{ eV}$  and recombination and diffusion density currents are about  $10^{-6} \text{ A/cm}^2$  and  $10^{-8} \text{ A/cm}^2$ , respectively, in agreement with the results of Ebarra group [9,10]

The photovoltaic parameters of  $4 \text{ cm}^2$  RJC cells made with a  $300 \mu\text{m}$  thick raw wafer and an evaporated aluminium layer are:  $V_{oc} \sim 560 \text{ mV}$  and  $J_{sc} \sim 16 \text{ mA/cm}^2$  without antireflection coating. Notice that for such a solar cell PC1D predicts a photocurrent density around  $17 \text{ mA/cm}^2$ , which is in good agreement with the experimental value.

Using a  $200 \mu\text{m}$  thick wafer (chemically thinned) the photocurrent reaches  $24 \text{ mA/cm}^2$ . With a screen printed Al layer, a  $300 \mu\text{m}$  thick wafer and a  $22 \text{ cm}^2$  RJC we measure  $V_{co} \sim 590 \text{ mV}$  and  $J_{sc} \sim 16 \text{ mA/cm}^2$ . As shown by Figure 8, the LBIC technique works well at  $\lambda = 960 \text{ nm}$  when the cell is illuminated by the phosphorus diffused

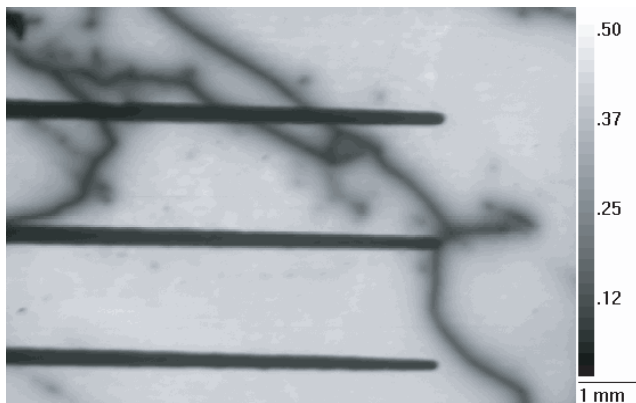


Fig. 8. LBIC contrast scan map of a RJC at  $\lambda = 960$  nm.

surface, although the thickness of the wafers is too large. The images of the grain boundaries are enlarged because the minority carriers must cross the entire wafer thickness before to be collected by the rear junction, but the grains appear very homogeneous, confirming that intra grain defects (dislocations and impurities) are poorly recombining.

## 4 Discussion

The preceding results confirm the high quality of  $n$ -type raw mc-Si wafers which exhibit very large values of lifetime and diffusion length of minority carriers. The high values of  $L_p$  are directly connected to the high values of  $\tau_p$  since the hole diffusion coefficient in the grains, computed from the expression  $L = (D\tau)^{1/2}$  is about  $10 \text{ cm}^2/\text{V s}$ , i.e. close to the conventional value in silicon. There is no doubt that it is due to the small capture cross section of metallic impurities which reduces the recombination strength of dissolved, precipitated and segregated impurities. As a consequence crystallographic defects, especially dislocations and subgrain boundaries, are poorly active.

The capture cross section ratio evaluated in  $p$  and  $n$  type mc-Si wafers from lifetime is smaller than that deduced from DLTS measurements carried out in monocrystals, this can be explained by the influence of native impurities present in mc-Si, which is not negligible compared to that introduced by ion implantation. As an example, interstitial chromium (frequently found in mc-Si wafers) reduces the advantage of  $n$ -type material because  $\sigma_n \sim \sigma_p$  (2). Fe and Cr tend to form pairs with boron in  $p$ -type material which the capture cross sections are different from those of interstitial atoms. Moreover these pairs can be partly dissociated by sunlight irradiation leading to a very complex situation. Nevertheless the lifetime values measured in both type of mc-Si lead to a neat advantage for  $n$ -type material which could be very useful in solar grade material made from purified metallurgical silicon.

The high sensitivity of  $n$ -type wafers to gettering treatments, like phosphorus diffusion, is not due to particular properties related to the type of conduction or to the presence of phosphorus atoms as dopants. Like in  $p$ -type mc-Si

wafers the gettering treatments reduces the density of fast diffusers. Even if the concentrations of such impurities are of the same order in  $n$ -type as in  $p$ -type silicon after a given gettering treatment, their recombination strength is weaker in  $n$ -type, and the influence of impurity-defect interaction on the recombination strength of extended defects is smaller. As a consequence  $\tau_p$  and  $L_p$  achieve very high values in the raw material [1].

The results obtained for our solar cells are limited by the too large thickness of the raw wafers which reduces the photocurrent.  $L_p$  is not sufficiently large and gettering treatments are necessary when the wafer thickness exceeds  $200 \mu\text{m}$ . This assumption is confirmed by the agreement obtained between the measured photocurrent density and the value computed by PC1D. Moreover the results show that technical processes used to make solar cells with  $p$ -type wafers (phosphorus diffusion; screen printing of aluminium and aluminium-silicon alloying) work with  $n$ -type material, and that is an advantage of RJC (notice that for  $n$ -type base solar cells phosphorus diffusion passivates the front surface and contributes to obtain a good ohmic front grid, while backside Al-Si alloying forms the  $p^+n$  junction).

## 5 Conclusion

The results presented in this paper confirm that  $n$ -type multicrystalline silicon is a high quality material which the lifetime and diffusion length of minority carriers reach very high values: in raw wafers the mean values, averaged on a  $25 \text{ cm}^2$  area, are in the range  $80$  to  $120 \mu\text{s}$  and  $200$  to  $250 \mu\text{m}$ , respectively. These values are still higher in gettered wafers, after phosphorus diffusion or aluminium-silicon alloying. This results essentially from the low values of the recombination center capture cross sections due to metallic impurities. The scan maps of diffusion length and of lifetime of minority carriers show that the effects of the interactions between impurities and extended defects are strongly reduced in  $n$ -type multicrystalline silicon, compared to  $p$ -type, and consequently the recombination strength of grain boundaries and of dislocations, although their concentrations could be very high in some sample regions, is neatly lower.

Such material could be used to make solar cells with a rear junction made through aluminium doping after aluminium-silicon alloying.

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