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Is n-type multicrystalline silicon the best candidate for short-term high-efficiency lower-cost solar cells?

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Abstract. In this article we detail a theoretical and experimental investigation in order to reveal the advantageous properties of multicrystalline n-type silicon for lower-cost high-quality solar cells applications. In this study, electronic grade (EG) and compensated upgraded metallurgical grade (UMG) materials are analyzed.
Three microwave-based contactless techniques (Microwave Photoconductivity Decay "µw-PCD", Microwave Phase-Shift "µw-PS" and Large-Scale Microwave Phase-Shift "LS-µw-PS") are applied to determine the carrier lifetime behaviour in an entire EG silicon ingot. We show that, at low injection conditions, the minority carrier lifetime profile is not directly related to resistivity variation along the ingot height. The carrier lifetime variation observed in all three techniques is related to Shockley-Read-Hall recombination process.
In compensated UMG silicon a higher minority carrier lifetime is observed in n-type than p-type area at the same conditions of contamination and injection level.

Key words

N-type multicrystalline silicon, minority carrier lifetime, contactless characterization, high-efficiency low-cost solar cells.

Introduction

Solar photovoltaic technology emerged as an important tool for sustainable and environmentally acceptable generation of electricity. Their potential applications are unlimited, making them the hope of future power supply concepts. Their great advantages are modular construction and availability everywhere. Additionally, in the near future, the cost of generating and transmitting this renewable energy would be less than the projected cost per kilowatt-hour for fossil-fuel and nuclear power [1]. And, a massive shift from conventional to clean power would lead to a 30 percent decrease in global power demand [2].

To enable this shift, reduction in material consumption and simultaneous improvement of the performance of solar cells are needed, producing a simple technology that can be implemented on a large scale. The best way to attempt this goal, in short-term, is continuous further development of well-tried, well-established technology and consistent implementation of new promising approaches.

In this scenario, crystalline silicon, in particular n-type silicon, is a great candidate because the potential of this reliable material is certainly not exhausted yet and the next generation of technology is just starting to enter the market. At present, almost 90% of worldwide solar cells fabrication is based on crystalline silicon technology and most of these cells are produced from p-type silicon. However, the well-establish p-type solar cell technology is most subject to light–induced degradation (LID) than n-type technology. It could be attributed to the formation of a boron–oxygen complex, which is highly recombination active [3]. This phenomenon appears to be less critical in n-type silicon. In low-cost silicon feedstock materials, like compensated upgraded metallurgical grade (UMG) silicon, investigations have been applied to determine the influence of boron complex formations over solar cells performances. In addition, n-type silicon was reported to be a material with higher carrier lifetime [4] due to the reduced sensibility towards the most of the metallic impurities compared to p-type silicon due to a reduced capture cross-section for minority carriers [5,6].

The minority carrier lifetime is the most important parameter to characterize the quality of silicon used in photovoltaic applications. A precise determination of the behaviour of physical properties of the silicon ingots requires measurement techniques that offer a clear comprehension of carrier interactions in the material. The defect characterization in silicon wafers permits the identification of recombination centres (impurities, dislocations, grains boundaries etc.) [7-9]. This procedure allows us to establish a plan of action to reduce or eliminate recombinant-active defects, providing a reasonable start-point for solar cells process and performance optimization.

Microwave-based minority carrier lifetime measurements techniques

Carrier lifetime measurements represent the time dependence of the excess carrier density within the semiconductors. This excess carrier density can be directly monitored via the photoconductance measured by means of the reflectivity of microwaves. The fundamental characteristics of these detection techniques will be discussed in the following paragraphs.

The microwave photoconductive decay (μw-PCD), a pure transient technique, is the most common contactless lifetime measurement. The effective carrier lifetime (τ_{eff}) is determined from the asymptotic decay of the average excess carrier density following a pulse-like excitation. This decay is monitored via the changes in the sample photoconductance which in turn is measured via changes in its microwave reflectance. It's fundamental to distinguish two principal contributions to τ_{eff} :

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \frac{1}{\tau_S} \quad (1)$$

where τ_b is related to recombination and trapping processes in the semiconductor bulk and τ_S refers to surface recombination velocity and sample thickness characteristics. This technique gives an effective value of the lifetime, which combines the effects of bulk and surface recombination centres. The relationship between τ_{eff}, τ_b, and S can be expressed by:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \left(\frac{W}{2S} + \frac{W^2}{\pi^2 D}\right)^{-1} \quad (2)$$

The modelling of effective carrier lifetime determination by μw-PCD technique, showed in Figure 1, presents the influence of wafer characteristics over lifetime measurements. Because τ_S is sensitive to the state of the surface, τ_{eff} is close to τ_b if an efficient passivation technique is applied in order to reduce the surface effects.

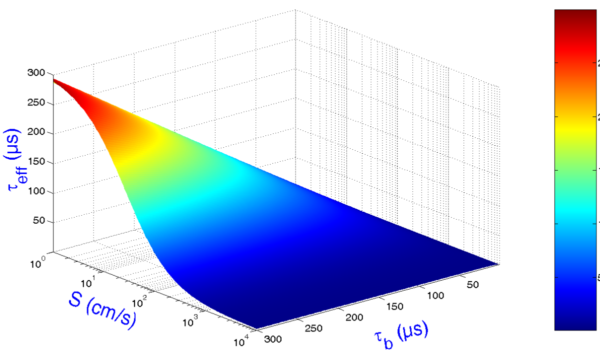


Figure 1: Modelling of effective carrier lifetime behaviour in function of bulk lifetime (τ_b) and surface recombination velocity (S) variations. Typical parameters to n-type silicon wafers have been used: D= 12cm^2/s and W= 160μm. S_f and S_b are considered equal.

Because the surface recombination velocity is a function of the injection level [10], a constant injection level is required during the lifetime investigation. This could be achieved using a weakly modulated exciting light instead of a pulse exciting light. For this purpose, in microwave phase-shift (μw-PS) [11] techniques, the sample is excited by a harmonic-modulated laser light so that the injection level is stable during all the measurements, thereby avoiding the problems connected to the surfaces. The phase-shift between the modulation and the microwave reflected by the sample is measured. From this phase-shift, the bulk lifetime as well as the surface recombination velocities of the illuminated side (front side), S_f, and of the back side, S_b, can be deduced by several measurements at different modulation frequencies.

According to the Orgeret and Boucher theory [9], the general law for phase-shift technique can be expressed by the following equation:

$$\Phi = f(\tau_b, S_f, S_b, D, W, \alpha, f) \quad (3)$$

Among the seven parameters of Eq. (3), four are known: the measured phase-shift (ϕ), the sample thickness (W), the absorption coefficient (α) and the modulation frequency (f). To determine x unknown parameters, the measurements must be repeated at x different frequencies. And, if we assume that S_f and S_b are equals (S_f=S_b=S), a double-frequency measurements gives the values of τ_b an S.

An illustration of this theory is presented in Figure 2. We can observe the modelling of the phase-shift (Φ) values obtained as a function of bulk lifetime variations for several frequencies of modulation. The others parameters influencing the phase-shift determination are fixed (D=12cm²/s, S_f=S_b=50cm/s, α=181.8cm^{-1} and W=160μm). A good choice of modulation frequency gives a better dynamic to phase-shift determinations.

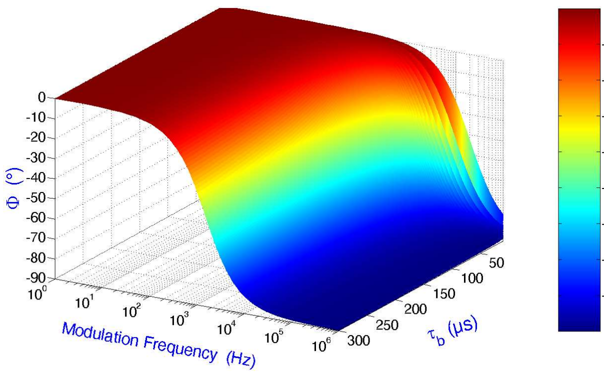


Figure 2: Modelling of phase-shift behaviour in function of bulk lifetime (τ_b) and sinusoidal modulation frequency (f) variations. Typical parameters to n-type silicon wafers have been used: D= 12cm^2/s, α=181.8cm^{-1} and W= 160μm. S_f and S_b are considered equal to 50cm/s.

Experimental Setup and Measures

A schematic representation of the apparatus for lifetime measurements is done in Figure 3. This experimental lifetime measurements setup uses the microwaves generated by a Gunn diode at 10 GHz as a probe. These microwaves are driven towards the bottom surface of the sample by means of a microwave guide. The excess carrier generation is provided by a fibre-coupled diode laser with a wavelength of 942 nm.

For µw-PCD measurements, this carrier generation is weakly pulse modulated at some ten hertz. In this case, we observe, thanks to an oscilloscope, an asymptotic decay of the average excess carrier density following a pulse-like modulation. In µw-PS measurements, a sine modulation in the range 0.5–100 kHz is used. The sinusoidal variation of the carrier density induces an identical variation of the reflectivity coefficient of the microwaves and thus the phase shift between the modulated exciting light and the reflected power of the microwaves is accurately measured thanks to a lock-in amplifier. Φ can be mapped with a spatial resolution better than 25 µm, which can lead to a S and τ_b mapping with the same spatial resolution.

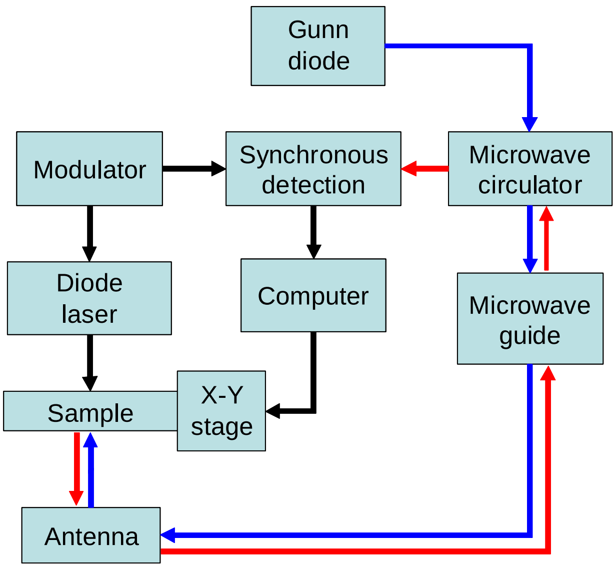


Figure 3: Schematic representation of the apparatus to lifetime measurements. The same set-up is used for µw-PCD and µw-PS techniques.

The measures were carried out on two different materials. The first one, is a n-type phosphorous doped (0.73 – 5.63Ω.cm) electronic grade (EG) multicrystalline silicon ingot. The interest in this type of material is justified by its low contaminants concentration that permits to highlight the principal electrical characteristic. Analyses are made over 14 wafers (wafer number 002 corresponds to the bottom of the ingot and number 391 corresponds to the top) of 160µm thickness, with an area of 125mm x 125mm, sampled along the entire ingot height and which have been previously passivated (SiNx) to reduce the surface effects. This passivation process allows us reach a quite homogeneous surface recombination velocity of ~50cm/s. The silicon wafers have been analyzed by three contactless microwave-based minority carrier lifetime measurements. These techniques allowed us to establish a profile of evolution of the minority carrier lifetime along the entire ingot and show the great potential of n-type multicrystalline silicon for high-efficiency lower-cost solar cells.

The second analysis concerns a compensated upgraded metallurgical grade (UMG) silicon. This material, contrary to EG silicon, contains several types of impurities, especially metallic contaminants. The presence and interaction between contaminants and dopants impurities define the electrical properties of this material along the ingot height during growth process and acts directly on the solar cell performance. During growth process the concentration of the dopants p and n changes due to different segregation coefficients for phosphorous and boron. It results in a type inversion along the ingot height, where the bottom is p-type and the top is n-type. The compensation phenomenon is always present along the ingot and a differential concentration of contaminants determines the local type and resistivity.

The principal aim of this study is observe the minority carrier lifetime behaviour in a wafer located at the polarity transition zone. In this case p-type and n-type co-exist in the same plane and are subject to the same impurities (non-dopants) concentration. To this, analyses with µw-PCD are made over a wafer of 200µm thickness, with an area of 20mm x 20mm, The zones p and n have been identified by means of a SEMILAB P/N conductivity type tester. This analysis enable a direct comparison between neighbour zones and highlights the superior effective carrier lifetime in n-type silicon material compared to p-type silicon at the same conditions.

Results and discussions

We present here the main results obtained from characterizations over silicon materials presented in the last paragraphs. At first, we evidence the minority carrier lifetime profile of n-type EG multicrystalline ingot. The main goal of this analysis is emphasizes the high quality characteristics of n-type silicon and reveal its potential for solar cells applications.

Carrier lifetime measurements have been performed by using µw-PCD technique (see Figure 4). In this case, all the samples have been passivated by SiNx in order to decrease the surface effects and move closer the measured effective carrier lifetime and bulk lifetime values. The surface recombination velocities (S), determined previously by µw-PS measurements, are around 50cm/s. The values presented in Figure 4 refer to the averaged value of the effective minority carrier lifetime observed upon scanning an area of 4cm² (20mm x 20mm) of the wafer. The minority carrier lifetimes measured are equivalent or higher than in typically p-type monocrystalline silicon wafers at the same injection level.

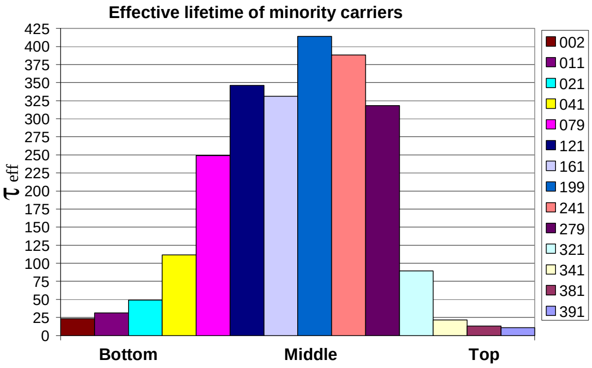
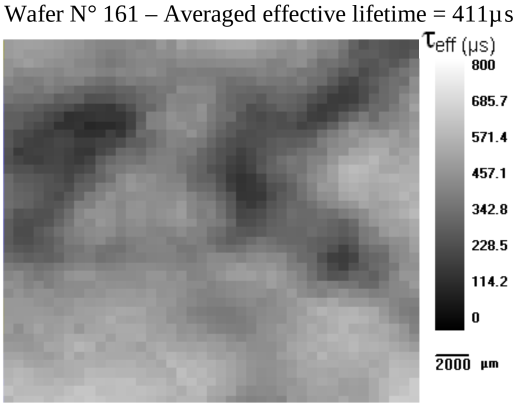


Figure 4: Evolution of the effective minority carrier lifetime along the ingot for n-type multicrystalline silicon samples, using µw-PCD technique.

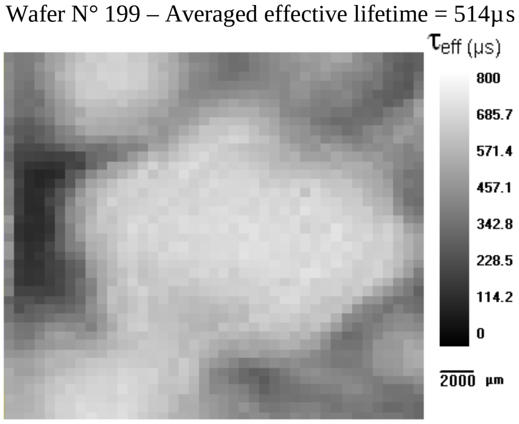
There is a "gaussian" behaviour of effective minority carrier lifetime observed along the height of the ingot, with a lifetime profile relatively uniform and higher in the middle of the ingot. This behaviour is related to the fact that in multicrystalline silicon the interaction between extended defects and impurities control the values of the lifetime of minority carriers (SRH recombination process). These defects are essentially related to ingot growth conditions (solidification rate, crystal defects, impurities contents and segregation phenomena).

The distance observed between the peaks of effective lifetime measured in consecutives wafers at the middle of the ingot are justified by the presence of grains whose effective lifetimes are longer than those of their neighbours. The size of these grains in comparison with scan sizes plays an important role on the averaged effective lifetime. This can be seen in details at Figure 5.

Wafer N° 161 – Averaged effective lifetime = 411µs



Wafer N° 199 – Averaged effective lifetime = 514µs



Wafer N° 241 – Averaged effective lifetime = 488µs

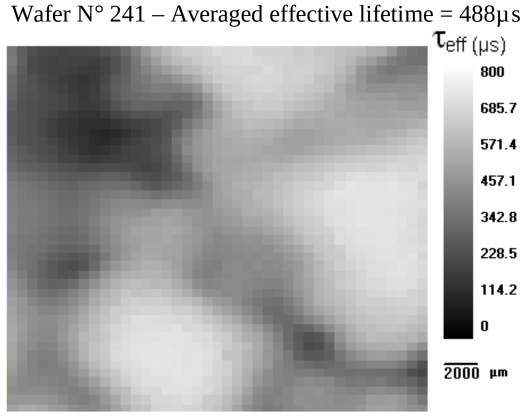


Figure 5: Effective carrier lifetime scanning maps (35mm x 35mm) in n-type multicrystalline EG silicon, obtained by µw-PCD technique.

The effective carrier lifetime evolution along the ingot is clearly independent of the resistivity profile along the ingot, as shown in Figure 6 and Figure 8. During the growth process, due to segregation coefficient of phosphorous, we observe an increasing concentration of dopants upward the ingot and a consequently decreasing of resistivity and mobility. Additionally, the segregation process of metallic impurities leads to a decreasing of carrier lifetime due to recombination process.

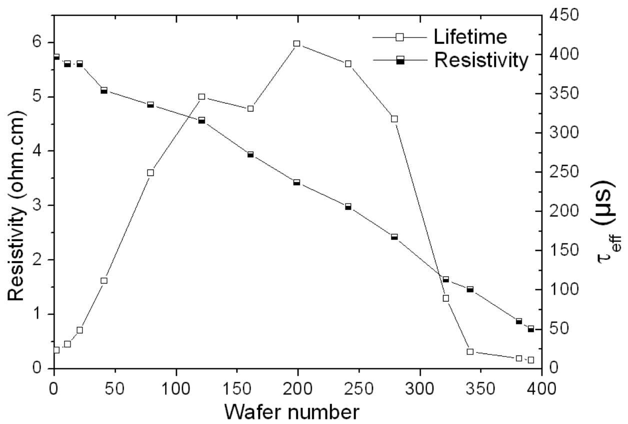
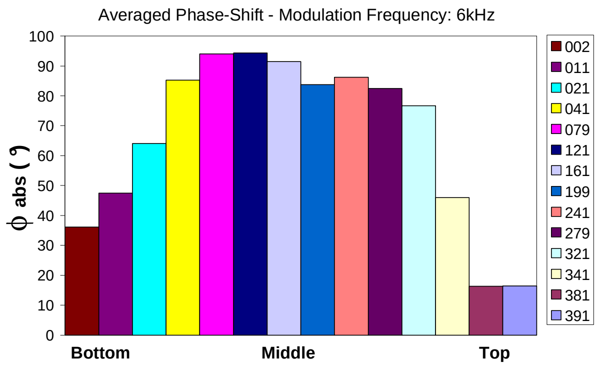
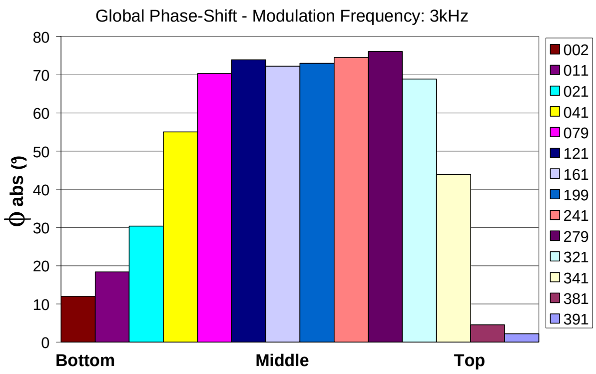


Figure 6: Resistivity profile and effective carrier lifetime evolution along the ingot height.

In order to confirm the effective carrier lifetime profile, observed by µw-PCD, along of the ingot we also made scanning maps of the same samples using the technique microwave phase-shift. Figure 7 shows the evolution of the phase-shift measured using two different measurement set-ups. In these techniques the phase-shift is directly related to the bulk lifetime (τ_b) of minority carriers and to the surface recombination velocity (S), as described in Eq. (3).



(a)



(b)

Figure 7: Evolution of the phase-shift along the n-type multicrystalline silicon ingot. (a) µw-PS technique and (b) LS-µw-PS Technique.

In the first case, we have used the µw-PS technique and the values presented refer to the average value of phase-shift obtained from a scanning area of 4cm² (20mm x 20mm) of the wafer. In the second case, we have applied the Large-Scale Microwave Phase-Shift technique and the values presented refer to the average value of phase-shift at a given frequency obtained at a global view on the entire sample (125mm x 125mm). We note the good agreement between the evolutions of the phase shift (related to variations in the lifetime of carriers) obtained by the two techniques. The evolution behaviour shown in Figure 7 confirms the results previously obtained by the µw-PCD technique. Notice that µw-PS can be used for any surface state whereas µw-PCD technique requires absolutely an efficient surface passivation.

The phase-shift profile obtained µw-PS along of the ingot permits us to establish a linear variation of ϕ in function of resistivity at the middle of the ingot, where the carrier lifetimes are less influenced by recombination process than at the top of the ingot, due to contaminants concentration. This is showed in Figure 8.

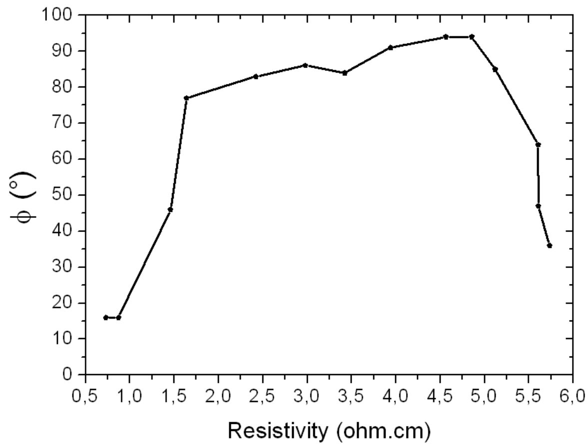


Figure 8: Phase-shift variation, obtained by µw-PS technique at 6 kHz, in function of resistivity profile at the ingot.

Additionally, we focus attention on effective minority carrier lifetime behaviour in a n-type compensated UMG multicrystalline wafer. The main goal of this analysis is emphasizes the robustness of a low-cost n-type silicon material for solar cell applications. In Figure 9 we show a lifetime scanning map over a compensated UMG silicon wafer, located in a transition zone of a ingot with type inversion. In this case, p-type and n-type silicon co-exist due to different segregations coefficients of impurities dopants during the growth process. By application of µw-PCD technique we can observe a higher effective carrier lifetime in n-type zone (light colours) that in p-type zone (dark colours). It demonstrates the lower sensitivity of n-type silicon than p-type silicon at the same impurity concentration. This leads to a carrier lifetime in n-type area that is at least five times higher than in p-type zone.

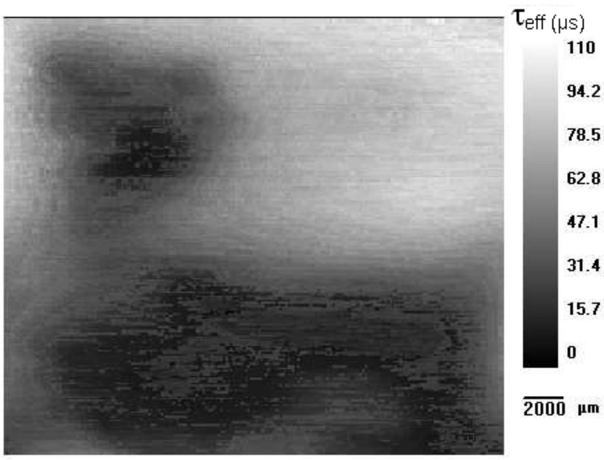


Figure 9:.Scanning map over a compensated UMG silicon wafer. Both p-type and n-type are present side-by-side.

Conclusions

N-type silicon material has presented high potential for high-efficiency solar cells applications. Superior carrier lifetime performance has been showed in n-type multicrystalline EG ingot. These measured carrier lifetimes are close to typical p-type monocrystalline silicon. This type of material could offer a better cost-benefit than p-type mono- and multicrystalline silicon.
To attempt costs reduction in material production and simultaneous improvement of the performance of solar

cells, compensated UMG silicon is a great candidate. In this material, carrier lifetime measurements have showed high performance in n-type zones. Lifetime values are at least five times higher than in p-type neighbour zone.
The implementation of a standard industrial process to n-type silicon technology in the near future will allow a complete exploitation of n-type silicon potentialities.

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