Millisecond minority carrier lifetimes in *n*-type multicrystalline silicon

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Exceptionally high minority carrier lifetimes have been measured in *n*-type multicrystalline silicon (mc-Si) grown by directional solidification and subjected to phosphorus gettering. The highest effective lifetimes, up to 1.6 ms averaged over several grains and 2.8 ms within some of them, were measured for relatively lowly doped, 2–3 Ωcm, wafers. The lifetime was found to decrease for lower resistivities, still reaching 500 μs for 0.9 Ωcm and 100 μs for 0.36 Ωcm. Several important findings are reported here: (i) achievement of carrier lifetimes in the millisecond range for mc-Si, (ii) effectiveness of phosphorus gettering in *n*-type mc-Si, and (iii) demonstration of good stability under illumination for *n*-type mc-Si. © *2002 American Institute of Physics.*
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Multicrystalline silicon (mc-Si) has become the prevalent material used by the solar cell industry, representing more than 50% of its total annual production. Different methods exist to fabricate mc-Si, usually in the form of large parallelepipeds that are cut into smaller ingots and then into wafers. The directional solidification method used in this work produces large mm to cm size, grains. Twins, dislocations, and other crystallographic defects are, nevertheless, common within the grains. In addition, metallic impurities, carbon, and oxygen are usually present. Industrially manufactured mc-Si is predominantly *p* type and boron doped. The simultaneous presence of boron and oxygen can lead to a bistable effect whereby the lifetime degrades upon exposure to natural or artificial light. This effect is a serious limitation for Czochralski (CZ) grown *p*-type, boron-doped silicon. A similar light induced degradation has also been documented for some mc-Si materials.[1] These results may not be directly extrapolated to other types of mc-Si since, in some processes, the oxygen content can be kept relatively low, thus decreasing the risk of degradation. In any case, a more robust solution to the degradation problem is to use *n*-type material, whose stability has been proven for CZ silicon, irrespective of its oxygen content.[2] The study of the electronic properties of *n*-type mc-Si presented here indicates that the quality of this material is, or can be made, exceptional.

Specific processing steps, including phosphorus diffusion and aluminum alloying, have a cleansing effect and are able to remove metallic contaminants from the silicon wafers, thus improving their lifetime. Such gettering techniques are present in some form in most commercial fabrication processes. They have always been behind the record efficiencies and lifetimes reported for mc-Si. Among the latter, for *p*-type mc-Si, it is worth noting intragrain minority carrier lifetimes of up to 135 μs for 0.65 Ωcm (Ref. 3) and 190 μs for 0.8 Ωcm.[4] Nagel *et al.*[1] measured an average lifetime of 140 μs for 1 Ωcm using a microwave detected photoconductive decay (PCD) technique, with some grains showing 400 μs. Our own quasisteady-state measurements of *p*-type mc-Si include effective lifetimes up to 260 μs in 1.5 Ωcm material, averaged over several grains.[5] The separation between surface and bulk recombination indicated a bulk lifetime of 600 μs.[6]

The *n*-type mc-Si studied here was grown at Eurosolare SpA in a commercial directional solidification furnace following the standard conditions used for the production of *p*-type ingots. The growth conditions used were similar to those of the conventional boron-doped material. The silicon feedstock consisted of the top and tail parts of electronic quality CZ Si ingots, both *n* type and, to a smaller extent, *p* type. The *n*-type conductivity of the mc-Si ingot, which we verified by the hot point probe test, was the result of light compensation between both dopant types. As a consequence of the low segregation coefficient of phosphorus (0.35, compared to 0.8 for boron), the concentration of phosphorus along *n*-type ingots, both CZ-Si and mc-Si, is not uniform and increases in the direction of the solidification. As shown in Fig. 1, the resistivity measured as a function of wafer position within the mc-Si ingot varies from approximately 3 Ωcm at the bottom to 0.33 Ωcm at the top. Whereas the 12.5 cm long ingot yielded a total of 250 wafers, only 50 wafers (one out of every five) are included in Fig. 1. The resistivity was measured with the same contactless conductance instrument used for the minority carrier lifetime measurements described next.

The 100 cm^2 wafers from Eurosolare were cut in smaller pieces of about 25 cm^2 for processing and etched in a mixture of nitric and hydrofluoric acids to remove possible surface damage and contamination. Some samples received a phosphorus gettering at 880 °C for 1 h using a relatively high $POCl_3$ concentration ratio in the diffusion furnace. This 40–55 Ω/sq diffusion was subsequently etched and a new light phosphorus diffusion at 840 °C, was performed to create 250 Ω/sq *n*-type regions on both sides of the samples. A thin oxide was thermally grown at 880 °C for 20 min in the same furnace, followed by a 400 °C anneal in a forming gas

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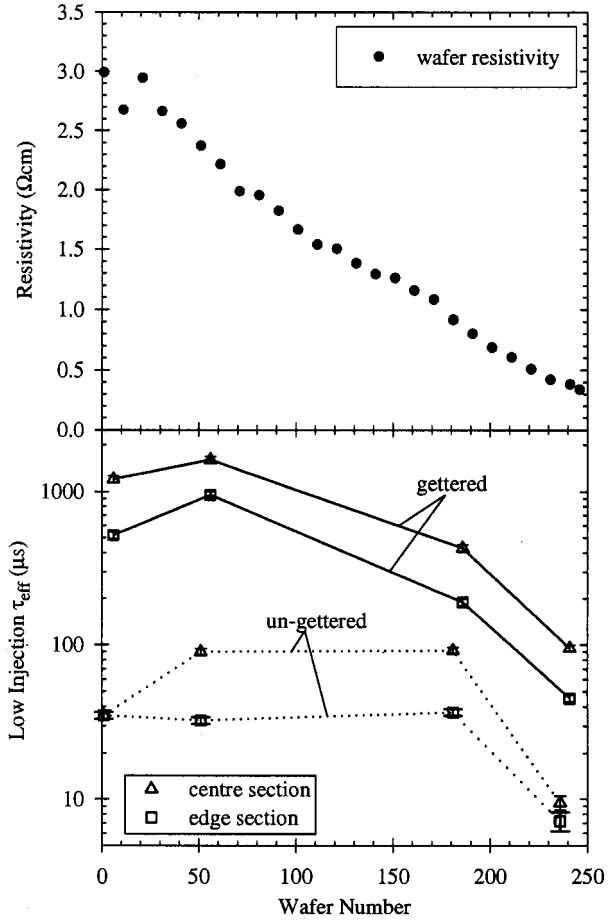

FIG. 1. Variation of the resistivity and τ_{eff} of *n*-type mc-Si as a function of ingot position, for both gettered and ungettered wafers. Samples were taken from both the edge and center of the ingot.

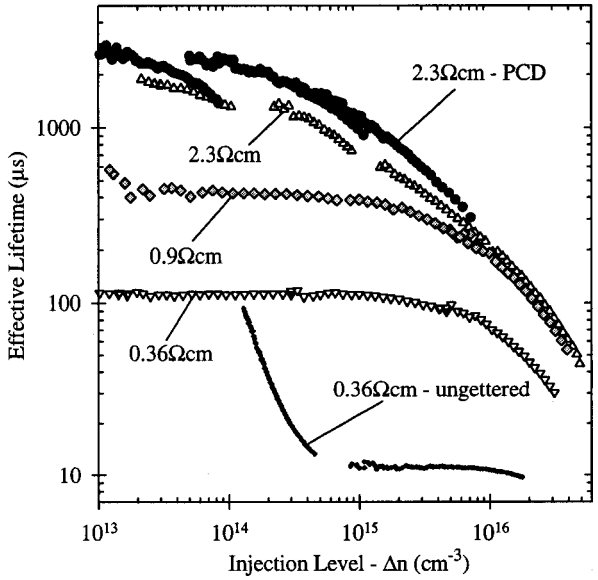

FIG. 2. Injection level dependence of τ_{eff} for gettered center sections of *n*-type mc-Si of different resistivities. All measurements are QSSPC with 4 ms flash, except the upper curve, labeled PCD. As shown for the 0.36 Ωcm case, phosphorus gettering greatly improves the lifetime and removes trapping centers.

(95% Ar, 5% H_2). The combination of a lightly diffused region and an oxidized surface minimizes surface recombination. Despite the passivation of the surfaces, their contribution cannot be totally discounted, and the lifetimes reported here should be considered as effective lifetimes.

The effective minority carrier lifetime of *n*-type mc-Si wafers from four different positions along the ingot, both with and without a gettering treatment, is also shown in Fig. 1. Without gettering, the lifetimes are in the range of 70 μs for 3 Ωcm material to 10 μs for the 0.36 Ωcm wafers. It is interesting to note that wafers nearest the bottom and the top of the ingot have a lower lifetime than those in the broad central region. After gettering, the bottom wafers essentially became identical to the lower center wafers which, in turn, reveal themselves to be superior to those from the upper center wafers. The effect of the phosphorus gettering was spectacular, with several wafers exceeding the millisecond lifetime mark, and all of them benefiting from it. The best result is for a 2.3 Ωcm wafer, whose average lifetime of 1.6 ms corresponds to a hole diffusion length of 1.4 mm. The lifetimes after gettering decrease with decreasing resistivity, a trend commonly seen in single-crystalline silicon. In particular, some 0.9 Ωcm wafers exhibited lifetimes of about 500 μs, and 0.36 Ωcm wafers; 100 μs.

The effective lifetime as a function of the excess carrier density is shown in Fig. 2 for several representative wafers. The 0.36 Ωcm ungettered wafer shows strong trapping at carrier densities below 10^{15} cm^{-3}. These trapping effects,[7] which are frequently associated with the presence of metallic impurities, disappear with the gettering treatment. The lifetime increases by a factor of 10 and remains practically constant over a broad range of injection levels, which is a very desirable feature for solar cell operation. A similar behavior is found for the postgettering lifetime of the 0.9 Ωcm wafer, except at high carrier densities where the lifetime is affected by Auger and emitter region recombination.

In the case of the 2.3 Ωcm wafer, also shown in Fig. 2, there is a significant difference between the lifetimes measured by either the photoconductance decay (PCD)[8] or the quasisteady-state photoconductance (QSSPC)[9] techniques, with PCD values of 2.8 ms, compared to 1.6 ms for the QSSPC lifetime. We have found a similar discrepancy between PCD and QSSPC lifetimes in *p*-type mc-Si.[6] The higher lifetimes obtained with the PCD method are representative of the best intragrain regions, while the QSSPC method gives an area-weighted average value over several grains. The sensing coil of the conductance instrument has a diameter of 2 cm and covers an area of approximately 3 cm^2 which, in all cases studied here, includes several grains and grain boundaries. The QSSPC method is based on the balance between generation and recombination, while the illumination on the sample is varied slowly. In this study, we have used a xenon flash that varies exponentially with a characteristic rate of 4 ms and has a total duration of 12 ms. Neutral density filters were used to attenuate the light and explore a broad range of light intensities. Using a control high resistivity float zone (FZ) wafer, we also measured the saturation current density of the two light phosphorus diffusions present at the surfaces of these wafers, $J_{oe} = 50$ fA/cm^2. This imposes a limit of 3.2 ms on the measurable lifetime in a 2.3 Ωcm *n*-type wafer, which indicates that

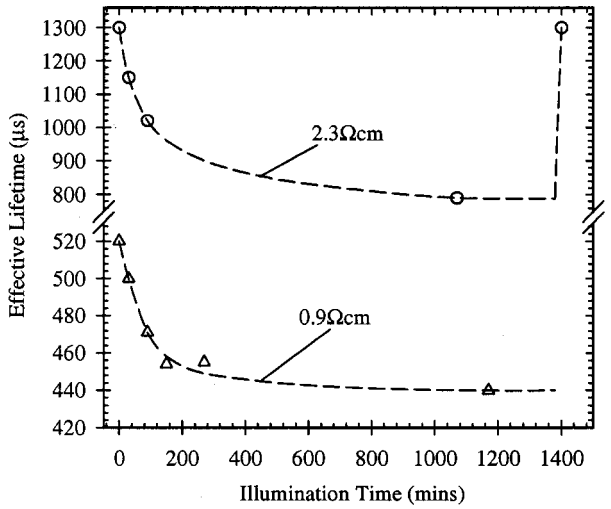

FIG. 3. Light induced degradation in gettered *n*-type mc-Si. The degradation is quite mild with stable effective lifetimes of 440 μs and 800 μs measured for 0.9 Ω cm and 2.3 Ω cm materials, respectively. The lifetime of the 2.3 Ω cm sample recovered after a 400 °C anneal.

the 1.6 ms average and 2.8 ms intragrain lifetimes are probably surface limited.

Light exposure experiments where carried out to evaluate the stability of the measured lifetimes. Selected mc-Si wafers were exposed to light from a halogen lamp with an intensity equivalent to the standard solar spectrum (100 mW/cm^2), while maintaining their temperature at 25 ± 2 °C. A FZ control wafer with identical surface conditions (light phosphorus diffusion and oxidation) was also exposed to verify that the passivation did not suffer any degradation. Lifetime measurements were taken at regular intervals, as shown in Fig. 3. A relatively mild degradation was observed for a 2.3 Ωcm wafer, with its maximum lifetime dropping from 1.3 to 0.8 ms after 18 h of light exposure. The lifetime fully recovered after a forming gas anneal at 400 °C, a behavior that is typical of the boron–oxygen complexes believed to be responsible for the light induced degradation of boron-doped CZ silicon. This recovery also excludes FeB pairs as a possible cause. The degradation observed in this *n*-type mc-Si may be thought to be associated with the residual boron still present in the wafers, together with a concentration of oxygen that tends to be highest at the bottom of the mc-Si ingots. Nevertheless, it is logical to expect that the concentration of boron should be much lower (probably by more than a factor of 10) than that of phosphorus, that is, lower than 2×10^{15} cm^{-3} in this *n*-type wafer. CZ silicon doped with a similar amount of boron would have a resistivity of 7 Ωcm and suffer a lifetime degradation of about 50%.[10] A 0.9 Ωcm sample from the upper part of the ingot degraded only marginally, from 530 to 440 μs after 19.5 h. The stable lifetimes of up to 800 μs and 440 μs are at a sufficiently high level as to consider *n*-type mc-Si stable in practice. In comparison, measurements by Nagel *et al.*[1] of 1 Ωcm *p*-type mc-Si showed a degradation from 140 to 70 μs. The lifetime of 1 Ωcm boron-doped CZ silicon typically degrades by more than a factor of 5, with final lifetimes of 10–20 μs.[10]

The minority carrier lifetimes for the *n*-type mc-Si material of different resistivities measured here are truly exceptional, reaching similar levels to *n*-type monocrystalline silicon, which are in the range of 1.1–6 ms for 0.6–1.5 Ωcm.[11] They prove that high-quality mc-Si can be grown by simple methods, using reject silicon, in commercial furnaces. The 0.5–1.6 ms average lifetimes measured in phosphorus gettered wafers with resistivities in the 0.9–3 Ωcm range imply minority carrier diffusion lengths greater than 0.7 mm, that is, more than three times the typical final wafer thickness. These results open the way for a class of silicon solar cells based on *n*-type mc-Si. High efficiency devices, including rear junction and bifacial designs, are certainly feasible using material of such quality. Based on the experiments presented here, these devices should be stable under illumination.

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