Response of *n*-type mc-Si to large variations of gettering and hydrogenation

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Abstract

The minority charge carrier recombination behaviour of *n*-type multicrystalline silicon wafers was systematically studied through microwave detected photoconductance decay, on as-grown samples, on samples submitted to phosphorus diffusion step and on samples after gettering and hydrogenation processes. First, we show that extreme gettering parameters (high temperature, high phosphorous-dosing of the wafer surface, long process) result in a significantly better cleaning of the edge zone of ingots, compared to typical phosphorous emitter diffusion. On the other hand, it results in less cleaning of the bulk silicon matrix, and somewhat more decoration of extended crystal defects. Second, we show that there is much improvement possible by enhanced hydrogenation of the wafer. This improvement applies to extended crystal defects but especially to bulk silicon matrix. Bulk silicon lifetime (in low defect crystals) continues to improve with increasing hydrogenation, in the wafers that we investigated e.g. from values around 150 µs after typical industrial hydrogenation, to 270 µs after the highest hydrogenation dose which we investigated.

Introduction

It is well known that the directionally solidified multicrystalline silicon (mc-Si) has become a dominant material in the fast growing photovoltaic market for solar cells because of its cost-effectiveness and excellent electronic properties. Nowadays commercial *p*-type mc-Si based solar cells achieve solar conversion efficiencies in the range of 15–16 % with industrial standard screen printing processes, up to 17 % with improved processes [1] and above 20% with more sophisticated solar cell designs [2–4]. Recently, *n*-type mc-Si has attracted attention as a short term solution to the main current problem for the photovoltaic industry: the silicon supply. A partial solution not yet on the market, is in fact the use of the *n*-doped silicon waste available from the semiconductor industry. Interest in *n*-type silicon is also growing due to the light-induced degradation problems associated with boron doped, oxygenated materials. Several benefits of *n*-type silicon wafers for solar cell applications have been reported recently [5–8], with the realization that *n*-type silicon is potentially more suitable than *p*-type silicon for high-efficiency commercial silicon solar cells. The high lifetimes measured for *n*-type multicrystalline and CZ silicon make innovative solar cells possible. It is important to note, however, that the measured lifetime was found to vary markedly across the surface of the wafer, with lifetimes ten times lower than the maximum values being common [5]. Since a large surface variability of this parameter is detrimental for large area devices, it is then convenient to characterize the effect of any kind of processing, as diffusion, passivation and firing, in terms of lifetime mapping or imaging.

Recent solar cell research has focused on material and process requirements for *n*-type solar cells, but some unknowns, concerning the specific role of certain impurities in a boron-free material and that of their interaction with extended defects, still remain. Since it has definitely been proven that in *p*-type mc-Si both the phosphorus diffusion and the contact firing through the silicon nitride improve the overall carrier lifetime and the material quality due to external gettering and bulk passivation respectively [for recent work see e.g. 9-11], we focused our investigations on the effect of phosphorus gettering and hydrogen passivation on bulk lifetime and crystal defects of neighbour *n*-type mc-Si wafers. We characterized the samples by mapping the recombination lifetime using the microwave photoconductance decay technique (µW-PCD) (Semilab WT2000 [12]).
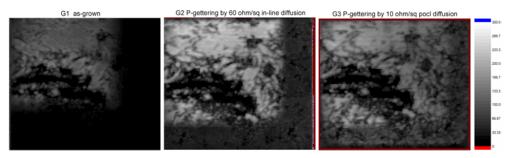
Experimental and discussion

A batch of neighbouring (12.5x12.5) cm^2, 0.6 Ω cm, <100>, *n*-type multi-crystalline silicon wafers were wet-chemically saw-damage etched and industrially cleaned. The wafers originated from the bottom of an edge block. The final thickness of the samples was around 250 µm. The batch was divided in 6 groups as explained in the following table. The G1 group is the reference group, representing the starting material quality. The G2 group simulates the industrial standard phosphorus diffusion / gettering process. The G3 group shows the effect of an extreme phosphorus gettering by POCl$_3$ diffusion. The G4 group investigates the hydrogen passivation by itself without gettering. In the G5 and G6 groups the wafers are both phosphorus gettered and hydrogenated. Within the G5 group the hydrogenation was fixed and the *pocl* diffusion was varied, in the G6 group the phosphorus gettering was fixed and the hydrogenation process was varied. The last two steps are applied at each group to passivate the surfaces before the bulk lifetime measurement.

Table 1: Processing groups distinctions.

Process Step	G1	G2	G3	G4	G5	G6
in-line diffusion	-	X	-	-	-	-
POCl$_3$ diffusion	-	-	X	-	X	X
PSG removal	-	X	X	-	X	X
SiN$_x$	-	X	-	X	X	X
Firing	-	X	-	X	X	X
SiN$_x$ + doped layer etching	-	X	-	X	X	X
HF dip + SiN$_x$	X	X	X	X	X	X

Phosphorus gettering

Double side phosphorus diffusion was performed in two different ways. The wafers of the G2 group were received a spray-on P- deposition followed by an in-line P-diffusion, using a Despatch spray-coater system to deposit phosphorus and a Despatch Infra-Red (IR) belt furnace to diffuse the doping impurities through the wafers, resulting in typical industrial in-line diffusion with an emitter with sheet resistance value of 60 Ω/ sq [13]. The samples of the G3 group were processed using a Tempress quartz tube furnace [14] at extreme conditions: heavy POCl$_3$ concentration, high temperature and long process, resulting in a doped layer with sheet resistance value of 10 Ω/ sq. The sheet resistance of the doped layers was measured using a four-point probe scanning tool [15]. The samples underwent a HF dip to strip off the SiO$_2$, and the doped layers were then etched and the wafers were industrially cleaned and subjected to a HF dip prior to the silicon nitride deposition. The SiN$_x$ layers were deposited on both sides of the samples, one side at a time, using a Roth & Rau PECVD system [16]. The samples were then characterized using the μW-PCD lifetime testing techniques [12]. In Figure 1 the sample lifetime maps are showed.
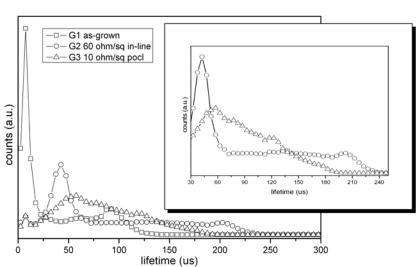

Figure 1: Lifetime maps of effects of gettering. Top: as-grown (left); typical 'industrial in-line diffusion' (60 Ω/sq) (middle); heavy (10 Ω/sq) pocl diffusion (right). Bottom: histogram distribution comparison.
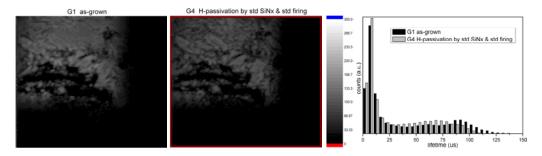
As expected, the average lifetime increases after the P-diffusion process, which induces impurity gettering effects at the external surfaces, but an evident local increase of electrical activity of some grain-boundaries was also observed. Apparently, a redistribution of impurities occurs at the processing temperature and impurities are captured at the deepest sinks. In fact, while the grain-boundaries act as heterogeneous segregation/precipitation sites, some of them will compete with the external surfaces as sinks, partly vanishing the effect of P-gettering. The extreme gettering parameters result in a significantly better cleaning of the edge zone of ingots, compared to typical phosphorous emitter diffusion. On the other hand, it results in less cleaning of the bulk silicon matrix, comparing with the in-line standard diffusion. This indicates, once more, that the effectiveness of the phosphorus gettering is determined by several external parameters such as segregation ratio to gettering layer, dissolution and diffusivity of impurities, etc., as well as by the internal wafer parameters such as

original state and density of the impurities in the silicon. The histogram peak moves to higher lifetime values either with the low temperature and fast diffusion, around 40 µs, or the extreme conditions: high phosphorus concentration, high temperature and slow process, around 60 µs. The 60 Ω/sq emitter results in a less uniform lifetime map compare to the 10 Ω/sq one, but it gives lifetime values greater than 200 µs in some areas.

Hydrogen passivation

To evaluate the individual effect of the hydrogen passivation, the wafers of the G4 group, after the saw damage removal and the industrial cleaning, were received an HF dip just before the double sided silicon nitride deposition [16]. The thickness and the composition of the deposited layers are that used in a standard solar cell line. Then, before the lifetime characterization, the wafers were processed in an IR belt furnace [13], with typical industrial firing step. The Figure 2 shows that, quite surprising given the results (presented later) of hydrogenation in combination with gettering, the hydrogenation process by itself does not result in an improved bulk lifetime. It might be that the diffused hydrogen content is not enough to clean the edges, to improve the bulk and to passivate the crystal defects. It also could be that a redistribution of mobile impurities is happening. Further investigations are needed to understand this.

Figure 2: *Lifetime maps of effects of hydrogenation. Left: as-grown. Middle: industrial silicon nitride and firing. Right: histogram distribution comparison.*

Phosphorus gettering and hydrogen passivation

It may be possible to still enhance the minority carrier lifetime of the material and, even more important, improve its spatial homogeneity by merging the phosphorus gettering with the hydrogenation process. To investigate the obtained sample lifetime when these two effects are combined we decided to act in the following way. We evaluated the effect of different gettering conditions by varying the phosphorus dose while using a standard industrial hydrogenation process. Then, having fixed the *pocl* diffusion recipe, we varied the hydrogen passivation process by changing the thickness of the deposited silicon nitride layer and modifying the firing step duration.

Effect of variation in gettering after standard hydrogenation

The main driving factors for phosphorus incorporation at given temperature are the percentage of the $POCl_3$ in the quartz tube and the (oxygen concentration) / ($POCl_3$ concentration) ratio. We decided to use a quite standard $POCl_3$ concentration (0.2%) and vary the oxygen dose. Moreover we used three drive-in temperatures and time. The samples of the G5 group, after a saw damage etching and an industrial cleaning, were double side diffused in a quartz tube furnace in three different conditions [14]. After a HF dip to remove the phosphorus silicon glass, we measured the conductivity of the doped layers by a sheet resistance scanning tool [15]. The measured sheet resistance values results in: 50 Ω/sq, 35 Ω/sq and 10 Ω/sq. Then the wafers after a HF dip received an industrial bulk hydrogen passivation, by a double side silicon nitride deposition followed by a typical firing step in an IR belt furnace [16, 13].
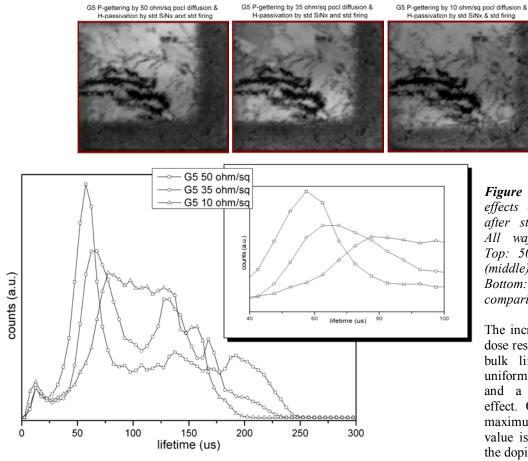
Figure 3: Lifetime maps of effects of gettering, evaluated after standard hydrogenation. All wafers POCl₃ diffusion. Top: 50 Ω/sq (left), 35 Ω/sq (middle), 10 Ω/sq (right). Bottom: histogram distribution comparison.
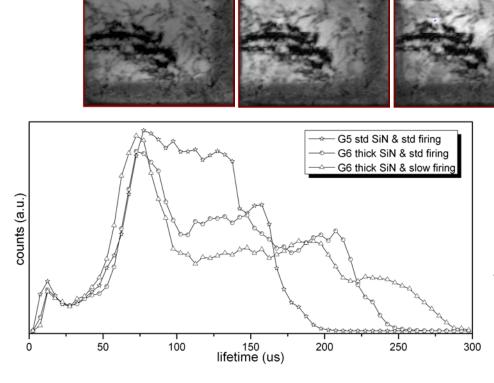
The increase of the phosphorus dose results in: a higher average bulk lifetime value, a more uniform lifetime distribution, and a better edge cleaning effect. On the other hand the maximum obtainable lifetime value is inversely correlated to the doping concentration.

Effect of increased hydrogenation

Figure 4: Lifetime maps after varying hydrogenation. All wafers the same (10 Ω/sq) POCl₃ diffusion. Top: typical 'industrial' hydrogenation (left), 3x thicker nitride, same firing parameters (middle), 3x thicker nitride, 3x slower belt speed used for firing (right). Bottom: histogram distribution comparison.

As it is widely known that the recombination activity of extended crystal defects strongly affects the electrical properties of the material and it is influenced by process-induced contamination, as shown in the previous paragraph, particular care was devoted in trying to passivate them by hydrogenation process. We used the double side [11] silicon nitride layers as source of atomic hydrogen and we diffuse these atoms by a high temperature and fast process using an infrared belt furnace [16, 13]. First, having fixed the 10 Ω/sq pocl diffusion recipe, we varied the hydrogen dose by simply depositing a thicker silicon nitride (3 times than standard one) layer, and then we tried to diffuse more hydrogen into the bulk by slowing the firing step time (3 times slower than standard one). So the wafers of the G6 group were processed as that one of the 10 Ω/sq G5 group up to the diffusion, and then were divided in two subgroups, one was processed with thicker SiNx followed by a normal firing, and the other with thicker SiNx and slower firing. The lifetime maps, Figure 4, show that the bulk passivation process is improving by increasing the diffused hydrogen dose. Since this effect is not equally effective in all areas, the homogeneity of the bulk lifetime is decreasing with the hydrogen increasing. Moreover the histogram peak of the sample with thicker SiNx and that received a slower firing is slightly moved to lower lifetime values (this effect can be originated from within the wafer itself).

Conclusion

The extreme phosphorus gettering parameters (high phosphorus concentration, high temperature, long process) result in a significantly better cleaning of the edge zone of ingots, compared to typical phosphorous emitter diffusion. On the other hand, it results in less cleaning of the bulk silicon matrix, and somewhat more decoration of extended crystal defects. Anyway there is much improvement possible by enhanced hydrogenation of the wafer. This improvement applies to extended crystal defects but especially to bulk silicon matrix. Recombination activity of extended crystal defects continues to decrease with increasing hydrogenation. Bulk silicon lifetime (in low defect crystals) also continues to improve, in the wafers that we investigated e.g. from values around 150 µs after typical industrial hydrogenation, to 270 µs after the highest hydrogenation dose which we investigated. On the other hand the lifetime spatial distribution is not improving with hydrogen content. Further investigation of different gettering conditions in combination with extended hydrogenation processes are foreseen as well as a comparison on the effect of the same kind of processes on *p*-type mc-Si wafers.

Acknowledgments

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