ALUMINIUM GETTERING IN POLYCRYSTALLINE SILICON SOLAR CELLS

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ABSTRACT

The influence of a thermal treatment of polycrystalline Si wafers on the performance of solar cells manufactured from these wafers is studied. The effect of the presence of screenprinted Al on the back of the wafer during the anneal and the influence of the anneal temperature are investigated. It is found that the efficiency of solar cells prepared from wafers with an Al doped layer on the back which were annealed at 700 °C is improved with 4% relative to cells prepared from wafers which did not receive such a treatment. The improvement occurs in the base but also in the surface region of the cell and is possibly mediated by Al which has diffused along grain boundaries to the top surface of the wafer.

INTRODUCTION

Large-grained polycrystalline silicon (poly-Si) is widely used as a low-cost material for the production of solar cells. However, the efficiency of these cells is limited by the material properties of poly-Si. Grain boundaries, low-angle sub-grain boundaries, twins and small physical defects as well as chemical impurities and impurity clusters have a deteriorating effect on minority carrier lifetime and diffusion length, and thus on solar cell efficiency. Several methods have been proposed to minimize losses caused by these effects. One of these methods is backside gettering by aluminium. Backside gettering by Al has been shown to improve the minority carrier diffusion length in poly-Si[1,2], and is expected to improve the efficiency of solar cells prepared from wafers which received such a treatment. This is a fortunate situation, because Al is already in use as a backside dopant to obtain a back surface field layer and a better ohmic contact with the backside metallization.

At present it is not clear whether the improvement is due to a real external gettering proces in the sense that impurities diffuse out of electrically important regions to a sink at the back of the cell or a passivating process caused by Al diffusion along grain boundaries followed by decoration and passivation of defects and impurities by Al. In this study, the effect of the presence of Al -deposited on the backside of poly-Si wafers- during a thermal treatment on the performance of large area poly-Si solar cells as well as the influence of the anneal temperature are investigated. All processes used are directly compatible with industrial solar cell manufacturing, in particular the Al-depositions which were performed using a screen-printing technique.

SOLAR CELL FABRICATION AND CHARACTERIZATION

Solar cells were manufactured using a standard production process. Starting material consists of Wacker SILSO p-type polycrystalline Si wafers of 10x10 cm^2. First an emitter is made by phosphorous in-diffusion. Al is screenprinted on the back and diffused in during a short thermal anneal. After removal of the remnants of the screen printed paste, the cell is completed with application of an anti-reflection coating (ARC) and front and back metallization. After diffusion of the emitter, wafers were divided into several statistically equivalent batches which

Table I. Experimental groups.

T_{anneal} (°C):	-	500	600	700	800
Control group :	St	C_{500}	C_{600}	C_{700}	C_{800}
Alloyed group :	St	A_{500}	A_{600}	A_{700}	A_{800}
Etched group :	St	E_{500}	E_{600}	E_{700}	E_{800}

all received a different treatment: Standard cells (St) received no extra treatment and were finished as described above. Control cells (C) were subjected to a thermal treatment of one hour before screenprinting of Al. Two experimental groups were subjected to the same thermal treatment, but after screenprinting and in-diffusion of Al: Alloyed cells (A) were heated directly after Al diffusion but before the remnants of the screenprinted paste were etched off; Etched cells (E) were annealed after this etch but before deposition of the ARC. The anneal temperature is indicated by a subscript, i.e. E_{500} denotes a batch of cells wich were annealed at 500 °C after removal of screenprint paste. A first experiment was performed on small batches of 25 cells which were subjected to temperatures of 500, 600, 700 and 800 °C for a time period of 1 hour. A second experiment consisted of a more detailed investigation of four selected larger batches of 75 cells, namely A_{500} and E_{700} plus the corresponding control groups. An overview of the experimental groups is given in Table I. In these proceedings we report results from both experiments. More results will be presented in a forthcoming paper[3].

All thermal treatments were performed in belt furnaces under flowing nitrogen; during the anneal the Si wafers were in contact with the Fe/Ni/Cr alloy constituting the transporting chain belt. In order to check whether this influenced the results, part of the cells was placed on clean Si pads which separated the metal belt from the wafers under study.

After completion, all cells were characterized by I(V) measurements. Both dark and illuminated (1000 W/m^2, AM 1.5) curves were measured as well as red and blue responses. For some selected cells, I(V) curves were analyzed using a 6-parameter fit[4] to 500 measured points on the curve. For all other cells, I(V) curves contained only 50 points and analysis comprised extraction of the short circuit current I_{sc}, open circuit voltage V_{oc}, fill factor FF, efficiency and two loss parameters due to series and shunt resistance. The shuntloss S is defined as $4.2 \bullet (I_{dark}/I_{sc}) \bullet 100\%$, where I_{dark} is taken at V=100 mV on the dark I(V) curve. S is a measure for the current leakage at the maximum power point and hence for the efficiency loss due to this leakage. From S, the shuntresistance R_{sh} can be estimated by $R_{sh} = 0.42 / (I_{sc} \bullet S / 100\%)$. Red and blue response (I_r and I_b) were determined by measuring the short circuit current while the cells were illuminated with either $\lambda > 600$ nm (red) or $\lambda < 600$ nm (blue) filtered 1000 W/m^2, AM1.5 light. Since for $\lambda = 600$ nm the optical penetration depth in Si is $\approx$2 µm, I_r is mainly determined by bulk properties in the base of the cell, while I_b is determined by the quality of emitter and depletion region.

RESULTS AND DISCUSSION

Results of I(V) measurements are shown in Figs. 1-3. Fig. 1 shows I_{sc} of the three groups C, A and E normalized with respect to the Standard group St as a function of anneal temperature. It can be seen that for group C, changes in I_{sc} are smaller than 0.5 % for all temperatures. For V_{oc} and FF we found a similar behaviour. This indicates that a thermal treatment alone has no deteriorating effect on solar cell performance, not even at a temperature of 800 °C. For the two experimental groups I_{sc} peaks at 500 °C (group A) and more clearly at 700 °C (group E). At 800 °C both A and E show a dramatic decrease. Since neither the peaks nor the decrease at 800 °C occur on the control group, these phenomena are considered to result from the presence of Al on the back during the thermal anneal. Fig. 2 shows the red response I_r of groups C, A and E normalized with respect to group St as a function of temperature. Again group C shows a behaviour which is independent of anneal temperature, whereas group E peaks at 700 °C and group A shows no change at 700 °C and a large decrease at 800 °C. Only one group, E_{700} shows a red response which is clearly higher than on group C, indicating that this is the only

Table II : Efficiency and standard deviation for some experimental groups

Group :	Standard	C_{500}	A_{500}	C_{700}	E_{700}
efficiency (%) :	9.62	9.84	8.53	9.71	10.04
SD(< average) :	0.66	0.47	1.00	0.40	0.51
SD(> average) :	0.30	0.32	0.91	0.31	0.29

treatment which improves the quality of the base material of the cell without simultaneous negative side-effects. Diode saturation currents as determined in the I(V)-fits showed a large spread due to random differences between the selected cells, still the first diode saturation current I_{01} was found on average to be lower for group E_{700} than for group St (not shown). I_{01} is a measure for the current losses due to recombination in the base of the cell[4]. This corroborates the conclusion drawn from Fig. 2 that the presence of Al on the back of a wafer during a thermal treatment at 700 °C improves the minority carrier diffusion length in the bulk material in the base of the cell.

The normalized shuntloss for groups C,A and E is shown in Fig. 3 as a function of temperature. Both experimental groups A and E show a decrease of the shuntloss with anneal temperature. Because group C shows almost no change in S, this difference is attributed to an effect of back-side Al. This is rather surprising, since Al is applied only to the back of the cell, and shuntlosses are determined by the quality of the junction on the front of the cell. In order to check whether the improved shuntloss observed in Fig. 3 is really due to an improved shuntresistance, more detailed I(V) curves consisting of 500 measured points per curve were determined for several equivalent cells from different batches and analyzed using a 6-parameter computer fit[4]. The shuntresistance estimated from the shuntloss was compared with the shuntresistance of the same cell, determined using the 6-parameter fit. A good correlation was found, indicating that the shuntloss determined from the simple I(V) analysis is a good measure for the shuntresistance. Thus it can be concluded that the improved shuntloss observed in Fig. 3 is indeed due to lower leakage across the junction. Further evidence for improvement of the surface region of cells in the group E_{700} is given by the observation of an increased blue-response for this group (not shown here). It is worthwhile to note here that backside gettering by Al as observed for group E_{700} minimizes a loss mechanism; the treatment is especially usefull on wafers which would produce cells with a large leakage if no gettering was used.

For group E_{700}, not only I_{sc} but also V_{oc} was found to be improved. This resulted in a marked increase in efficiency for this group, as can be seen in Table II. This table lists the efficiency and standard deviations for the standard group and for groups C_{500}, A_{500}, C_{700} and E_{700}. These values represent an average over 75 cells. Standard deviations were calculated separately for larger and smaller efficiencies than the average value. This was done because the distribution of cells over efficiency is not symmetrical around the average efficiency. It can be seen that for group E_{700} the efficiency is increased with 4% relative to the standard group, and that both deviations for smaller and larger efficiencies for E_{700} are somewhat decreased. The low efficiency of group A_{500} is contrary to our findings on the smaller groups of 25 cells. This group showed a very large shuntloss, which is most likely due to damage caused by repeated V_{oc} and R_{sheet} measurements in between the different processes in the solar cell fabrication sequence. These measurements were not performed during the first experiment. Why the other groups from the second experiment do not suffer from comparable losses is not clear. Although not listed in the table, no significant differences were found between cells annealed directly on the belt and cells annealed on Si pads to isolate the wafer from the metal belt.

In order to evaluate the possible mechanisms that can explain the results obtained thus far, grain boundary diffusion lengths for Al are shown in Table III for the temperatures involved.

Table III: Grain boundary diffusion distance during a thermal treatment of one hour for Al in polycrystalline Si, divided by cell thickness W. Data taken from Ref. 5.

T (°C) :	20	500	600	700	800
$\sqrt{Dt}/W$:	$4 \cdot 10^{-16}$	0.017	0.17	1.02	4.3

These values are extrapolated from data on grain boundary diffusion of Al in small grained polycrystalline Si[5]. It can be seen that for temperatures of 700 °C and higher, Al may diffuse all through the wafer and reach the emitter. It is not inconceivable that Al doping of grain boundaries occurs, shielding these boundaries for minority carriers and reducing recombination at the grain boundaries even close to the front surface. In addition, Al may diffuse via grain or sub-grain boundaries into the grains and decorate and/or passivate defects and impurities, thus reducing the number of active recombination centers. In this picture, both an improved red-response and a diminished junction leakage for Al backside gettered cells can be understood. Strictly speaking this is not a gettering but a passivating mechanism. However, external gettering processes such as defect or impurity diffusion out of the active regions of the cell into a sink formed by the Al doped layer at back of the cell cannot be excluded.

It is not clear why I_{sc} and I_r are decreased for A_{800} and E_{800} and not for C_{800}. An intuitive explanation would be short-circuiting of the junction by Al which must have diffused along grain boundaries up to the emitter, but this is not in agreement with the very low shuntloss observed for group E_{800}. Another possibility is that the screenprint paste introduces some chemical impurities which enter the wafer and become activated for temperatures in excess of 700 °C. In this context it is noted that the effect is larger for A_{800}, which was annealed with the screenprint paste still present on the back of the cell, than for E_{800}, where the paste was removed before anneal.

CONCLUSIONS

A thermal treatment of polycrystalline Si wafers with an Al doped layer at the back during one hour at 700 °C, improves the efficiency of solar cells made from these wafers with about 4% relative to solar cells made on wafers which did not receive such a treatment. This improvement is brought about both by improved bulk properties in the base of the cell, as can be concluded from an improved red response, and by improved junction characteristics, as can be concluded from lower junction leakage. Although impurity or defect diffusion out of the wafer into the doped layer as a gettering process in the strict sense of the word cannot be excluded, the main mechanism by which these improvements are mediated is suggested to be diffusion of Al along grain boundaries all through the wafer, followed by formation of a p^+ region around grain boundaries and/or decoration and passivation of defects and impurities by Al.

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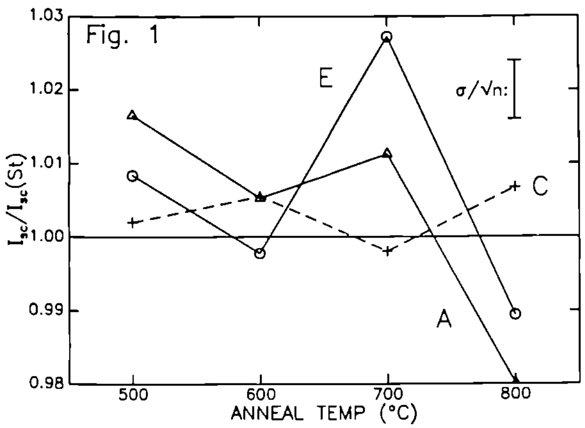

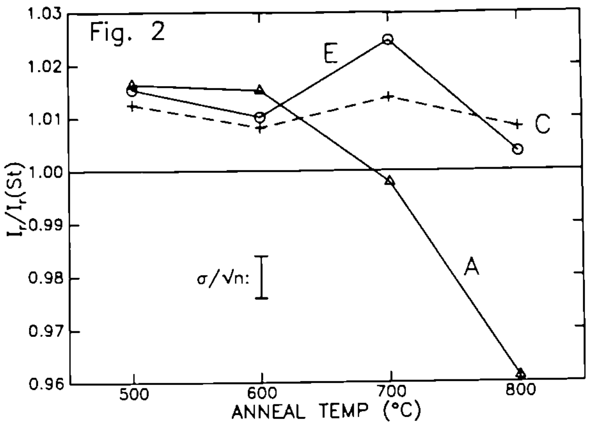

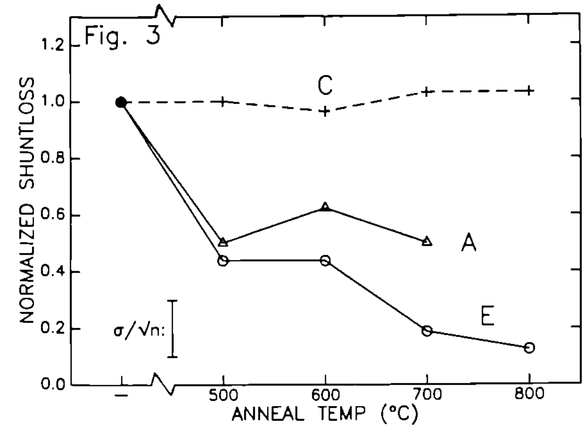

Figure 1. *Short circuit current for three experimental groups relative to standard cells as a function of anneal temperature. C = control group with no Al; A = annealed with screenprinted Al on the back; E = annealed after Al diffusion and removal of screenprint paste.*

Figure 2. *Red response for three experimental groups relative to standard cells as a function of anneal temperature. C = control group with no Al; A = annealed with screenprinted Al on the back; E = annealed after Al diffusion and removal of screenprint paste.*

Figure 3. *Normalized shuntloss for three experimental groups as a function of anneal temperature. C = control group with no Al; A = annealed with screenprinted Al on the back; E = annealed after Al diffusion and removal of screenprint paste.*