IMPROVED BULK AND EMITTER QUALITY BY BACK-SIDE ALUMINIUM DOPING AND ANNEALING OF POLYCRYSTALLINE SILICON SOLAR CELLS

L.A. Verhoef, S. Roorda, R.J.C. van Zolingen* and W.C. Sinke

FOM-Institute for Atomic- and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam
*R&S Renewable Energy Systems B.V., P.O.Box 45, 5600 AA Eindhoven
The Netherlands

ABSTRACT

The influence on solar-cell properties of thermal annealing polycrystalline silicon wafers was studied. Electrical performance and quantum efficiency measurements revealed that cells produced from wafers which received a one-hour anneal at 700 °C with an aluminium-doped back side exhibited a bulk diffusion length enhancement of 15 % over non-annealed cells. A 5 % bulk diffusion length improvement was found when Al was absent during the anneal. The blue response was improved compared to unannealed cells and was independent of emitter sheet resistance for cells with an Al-doped back side during the anneal. In standard cells and cells annealed without Al, this blue response decreased with increasing sheet resistance. These data suggest that in wafers with low emitter phosphorous concentration, aluminium takes over the passivating and/or gettering action of phosphorous. Aluminium presumably has reached the front side of the cell by grain-boundary diffusion through the entire wafer thickness, thereby passivating grain- and sub-grain boundaries.

INTRODUCTION

Polycrystalline silicon is widely used for the production of low-cost solar cells. In this material, crystal quality and minority-carrier recombination lifetime are lower compared to mono-crystalline silicon due to high concentrations of grain- and sub-grain boundaries, small physical defects and impurity clusters. Since solar cell-performance depends strongly on minority-carrier lifetime and diffusion length, several processes have been developed in the past to improve these transport parameters during the processing of solar cells.

Two of these processes are passivation (1) and gettering (2). Passivation requires temperatures high enough to enable diffusion of the passivating agent. The commonly accepted picture is that the passivators, hydrogen, lithium or others, bind to dangling bonds at the grain boundaries, thereby removing mid-gap recombination centers (3,4). Gettering requires a sink for impurity atoms and/or defects and temperatures high enough to enable impurity-diffusion and to mobilize defects. Dislocation-rich (5,6) and phosphorous doped regions (7,8,9) provide such sinks. Some authors have found that aluminium-alloyed regions improve the bulk recombination lifetime upon annealing (2,10,11) The nature of this mechanism has not yet been revealed. It has been suggested that the Si near the Al-Si interface contains high concentrations of vacancies, which can capture chemical or physical impurities (12). Another possibility is that Al diffuses along grain boundaries, thereby either preferentially doping these boundaries (the aluminium becomes electrically active) or passivating dangling bonds and other deep-level recombination centers (the aluminium is electrically inactive). In the first case, minority carriers are shielded from the recombination centers, in the latter case recombination sites are actually removed. Martinuzzi et. al. (2) have shown that in low-temperature anneals of 2 hours, 400 °C, the minority-carrier diffusion length was improved; at this temperature, the grain-boundary diffusivity of aluminium is too small (13) to enable extensive preferential diffusion and they assume that gettering of impurities (mobile at that temperature) or defects occurs.

Earlier, we published some indications that gettering or preferential diffusion of Al occurs during one-hour anneals at 700 °C of wafers containing aluminium-doped back sides(10). From the data we could not infer whether Al or the defects and impurities are the moving species during anneals at this temperature. The problem with discriminating between gettering (impurities and defects move) and passivation (Al moves) is that impurities supposedly gettered in the Al-doped Si layer are so low in concentration that few experimental techniques are capable of tracing them. It is also still unknown what the effect is of a combination of both phosphorous- and aluminium-gettering or passivation; then impurity sinks are present on both sides of the wafer during an anneal.

In this paper we present the results of annealing experiments on polycrystalline silicon solar cells, which shed some new light on these matters.

SOLAR CELL FABRICATION AND CHARACTERIZATION

Solar cells were fabricated on Wacker SILSO 10x10 cm^2 wafers, using a standard process. First an emitter is formed by phosphorous in-diffusion. Second, aluminium is screenprinted on the back-side of the wafers. An Al-Si alloy is obtained by a short anneal in a belt furnace. Subsequently the excess aluminium is etched away with HCl and finally,

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the anti-reflection (AR) coating and metallization pattern are applied.

Three statistically equivalent groups of 75 wafers were processed. The first two (E7, D7) were subjected to a one-hour anneal at 700 °C, the third was kept as a standard reference group (D0). Group E7 was annealed prior to applying the AR coating. This group contains a phosphorous doped emitter at the front side and an Al-doped region at the back side of the wafer during the anneal. Group D7 was annealed before applying the aluminium screen print. This group only contains a phosphorous doped emitter during the anneal. See table I for processing parameters.

Another experimental batch consisted of 5 statistically equivalent groups of 25 cells: e0, e5, e6, e7 and e8 which were subjected to no anneal (e0) and a one-hour anneal prior to the AR coating at 500, 600, 700 and 800 °C, respectively. These groups served to evaluate the role of the anneal temperature.

The sheet resistance (14) of the emitters was determined twice during the processing: first directly after phosphorous diffusion and a second time just before the AR-coating was applied. On all finished cells, short-circuit current I_{sc}, open cell voltage V_{oc}, fill factor FF and efficiency η were measured at simulated 1000 W/m^2 AM1.5. Cell temperature remained at 25 °C. To gain more insight in how cell performance had changed, the blue response I_{blue} (short-circuit current at filtered AM1.5,λ<600 nm) and red response I_{red} (short-circuit current at filtered AM1.5, λ>600 nm) were determined on all wafers. I_{blue} mainly probes the emitter region of the cell (because of the small penetration depth of light (< 2 μm) at these wavelengths) and I_{red} characterizes the bulk quality.

On a random set of 10 cells from each group, the quantum efficiency (number of electrons in external current per incoming photon of wavelength λ) was determined over a wavelength range from 366 to 1100 nm. A light-bias of approximately 0.15 Suns was used to saturate the minority-carrier traps. By light-biasing the cells, traps are filled by minority carriers, making these traps inactive as recombination sites; thereby the bulk diffusion length is improved. The effect of varying light-bias intensity on quantum efficiency was determined at one wavelength λ=940 nm for sets of 10 cells from groups D0, D7 and E7 to gain insight in the process of trap saturation in these groups.

RESULTS AND DISCUSSION

Sheet Resistance

For the three large groups, the relative change in sheet resistance upon Al-alloying, HCl-etching and AR coating is shown in table I. A negligible increase is observed in group D0, indicating no influence of the standard fabrication process on R_{sheet}. Group D7 exhibits practically no change in R_{sheet}, implying that a 700 °C thermal anneal in itself does not affect the total amount of electrically activated phosphorous. The effect of aluminium is apparent in group

Table I. Specification of the 3 large experimental groups and 4 small groups and relative change in sheet resistance due to alloying, annealing and HCl etching. Error in this change equal to 3.5 % absolute.

group	back side during anneal	# cells	anneal temperature	relative change in R_{sheet} (%)
e0		25	no anneal	
e5	Al-doped Si	25	500 °C	
e6	Al-doped Si	25	600 °C	
e7	Al-doped Si	25	700 °C	
e8	Al-doped Si	25	800 °C	
D0		75	no anneal	3.8
D7	bare Si	75	700 °C	1.2
E7	Al-doped Si	75	700 °C	20.0

E7: sheet resistance increases 20% upon annealing. This suggests that compensation of phosphorous by aluminium takes place in E7. The grain-boundary diffusivity at 700 °C, extrapolated from measurements by Hwang et. al. (13), is 300 μm/hr$^{1/2}$, large enough for diffusion of Al from back to front. Preferential diffusion of phosphorous along the grain boundaries or de-activation of phosphorous by formation of phosphorous complexes would also lead to an increase in R_{sheet}, but these effects should also occur in group D7, which is not observed. Similar changes in R_{sheet} have been observed in the groups e5, e6 and e7 (not shown). R_{sheet} of e8 remained at the same level as e0, possibly because apart from aluminium compensation, phosphorous diffusion takes place. The latter reduces the heavy doping in the emitter and enhances the product of activation, mobility and doping density, which is equal to the inverse sheet resistance.

Blue and red response

Data from the I(V) measurements and red- and blue response are shown in table II. I_{sc}, V_{oc}, FF and η are all improved in the E7 group compared to group D0. The increase in efficiency is mainly due to an increase of I_{sc} and to an improved fill-factor. The latter results from reduced junction leakage (10).

Table II, I(V) measurements under 1000 W/m^2 AM1.5 at 25 °C and blue (filtered AM1.5, λ<600 nm) and red (filtered AM1.5, λ>600 nm) response measurements on all groups; average over 75 cells per group. Typical standard deviations σ_n are shown in the first row.

group	I_{sc} (A)	V_{oc} (mV)	FF (%)	η (%)	I_{blue} (A)	I_{red} (A)
σ_n	0.060	4.0	2.3	0.40	0.020	0.040
D0	2.531	556.1	68.7	9.60	0.482	1.680
D7	2.515	559.3	69.2	9.71	0.475	1.706
E7	2.569	559.0	69.8	10.04	0.488	1.711

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D7 and E7 both display improved red response. This indicates an increase of the bulk diffusion length due to an anneal both in presence and absence of aluminium at the back surface. Only E7 has an improved blue response while I_{blue} of D7 is considerably lower than D0. The blue response is determined mainly by the top region of the cell, so the aluminium at the back side apparently affects the front of the cell.

The same trend as in E7 (improved I_{red} and I_{blue}) have been observed for anneals at 500 and 600 °C, see groups e5 and e6 in table III. The improved red response has been correlated to the aluminium grain-boundary diffusivity which is lower at 500 and 600 °C than at 700 °C (10). When the anneal is performed at higher temperatures (800 °C), thermal stress reduces the bulk diffusion length, resulting in a reduced red response.

Table III, Average (over 25 cells) blue response I_{blue} (filtered AM1.5, $\lambda<600$ nm) and red response I_{red} (filtered AM1.5, $\lambda>600$ nm) for the small cell groups annealed with Al doped silicon at the back at various temperatures. Standard deviation σ_n shown in first row.

group	I_{blue} (A)	I_{red} (A)
σ_n	0.015	0.050
e0	0.468	1.733
e5	0.462	1.759
e6	0.470	1.751
e7	0.470	1.776
e8	0.447	1.740

I_{blue} of e5 and e8 is smaller than that of e0, e6 and e7. The 600 and 700 °C groups show a blue response which is almost unchanged compared to e0. The lower blue response of e5 is possibly due to the small aluminium grain-boundary diffusivity (≈ 6 µm) because of which aluminium cannot reach the emitter. Apparently, the anneal in itself at 500 °C is detrimental for the emitter region. The reduced blue response when the anneal is performed at 800 °C is probably due to widening of the emitter by bulk and grain-boundary phosphorous diffusion. No indications of junction shunting have been found; on the contrary, the current loss due to shunt resistance and the space charge saturation current density (from a two-diode equivalent circuit (15)) were shown to be even lower after an 800 °C than after a 700 °C anneal.

The difference in absolute blue and red response of e7 and E7 arises from the fact that these groups are not statistically equivalent. Almost all cells in the small group e7 (and also in e5,e6 and e8) consist of large-grain material mainly, yielding efficiencies superior to E7. The small increase I_{blue} of e7 (only 0.4% larger than e0) in comparison with E7 (1.3% larger than D0) is within the experimental inaccuracy. However, the groups e0, e5, e6, e7 and e8 may be compared.

Quantum Efficiency

In order to get a more detailed understanding of the operating mechanisms, quantum efficiency (QE) measurements have been performed. The average over 10 cells of groups D0, D7 and E7 was determined. In figure 1 the QE of D7 and E7 normalized with respect to D0 is shown. Quantum efficiency of E7 is superior over D0 in the entire wavelength range. For group D7, QE is considerably smaller in the intermediate wavelength range, but larger for the infrared and the ultraviolet part. Thus annealing in itself has a negative effect on the junction region of the cell but improves the emitter and the bulk diffusion length. The presence of aluminium during annealing not only compensates the negative effect, but even improves both the bulk quality and emitter region compared to standard cells.

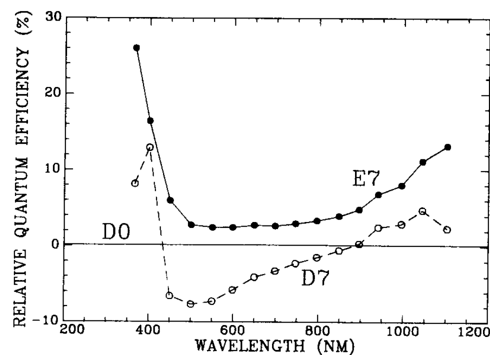

Figure 1. Quantum efficiency of groups D7 and E7 (both annealed for 1 hour at 700 °C) normalized with respect to the non-annealed reference group D0. The back side of group E7 was aluminium doped prior to the anneal.

The difference between D7 and E7 is not due to differences in anti-reflection coating, which would only amount to differences in current of a few percent per cell. Because 10 randomly selected cells of 100 cm^2 are averaged the differences are reduced to under 1 %. Systematic differences in the thickness of the anti-reflection coating between the various groups are estimated to yield deviations between two groups smaller than 1%.

The average diffusion length of the groups, as inferred from the infrared part of the spectral response are given in table IV. These diffusion lengths have been normalized because uncertainties in absorption coefficient data complicate absolute determination. Using different sets of absorption data (16,17,18,19) gives different values for the diffusion length but nearly the same relative improvement. Diffraction of light at the textured surfaces of our cells influences the effective penetration also obscuring

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Table IV. Bulk minority-carrier diffusion length for the various groups (see text), normalized with respect to the standard, non-annealed group D0.

group	T_{anneal} (°C)	$\frac{L_{diff}}{L_{D0}}$
D0	25	1.000
D7	700	1.048
E7	700	1.156

Table V, Effect of bias light intensity on quantum efficiency.

group	Intensity of max(suns)	$\frac{QE(max)}{QE(dark)}$
D0	0.3	1.06
D7	0.2	1.06
E7	0.2	1.04

absolute analysis. The bulk diffusion length after an anneal in presence of an aluminium back side at 700 °C, shows an increase of 15 % over standard cells. For group D7, which underwent a comparable anneal (1 hr, 700 °C) without aluminium, the average diffusion length showed a 5 % enhancement. Thus 10 % of the gain in bulk diffusion length of group E7 is attributed to the presence of aluminium. The diffusion length in all groups is still much smaller than the cell-thickness. Therefore improved back surface field action can be excluded as the origin of this enhanced diffusion length.

The influence of bias-light intensity on spectral response at 940 nm is given in table V. These are averages over 10 cells per group. The ratio of spectral response at that saturation intensity over spectral response in the dark (QE(max)/QE(dark) was significantly smaller for group E7 than for D0 (it should be noted here that 'dark' corresponds to an intensity of $2X10^{-3}$ suns). This ratio is equal for groups D7 and D0. Apparently, after an anneal on wafers with an aluminium-doped back side, the concentration of electrically active traps at the grain- and sub-grain boundaries is reduced, since only a small improvement results from trap-filling by light biasing. A thermal anneal alone does not seem to affect the trap concentration and activity, because saturation of the traps by minority carriers has the same effect as in not-annealed cells. But the anneal does influence the average diffusion length, which is larger in D7 than in D0. A redistribution of the density of states in the band-gap due to the anneal could account for this. For instance, the anneal could make the distribution of gap-states smaller and more peaked at the mid-gap energy.

We have indications that the spectral response saturates at a lower light intensity in D7 and E7 than in D0, see table V. For group E7, this would support the reduction or de-activation of traps by annealing in presence of aluminium: fewer traps are available to be filled. For group D7, it suggests a redistribution of gap states rather than a reduction, because no difference in the ratio (QE(max)/QE(dark) was observed for this group compared to D0.

The most surprising finding is the strong influence of back-side aluminium on the spectral response in the blue. In the 360-400 nm regime the QE of E7 is improved with more than 10 % in comparison to D0 and in 400-600 nm regime more than 10% in comparison to group D7. These results agree qualitatively with the measurements of I_{blue} (see table II), although the comparison is obscured by the fact that in D7 for wavelengths smaller than 450 nm the quantum efficiency is higher and for wavelengths larger than 450 nm it is smaller than that of D0. Convolution of the quantum efficiency with the spectrum of the blue filtered light, however, yields good agreement between the data. Similar results are found for the groups e5, e6 and e7 and e8.

Correlation of blue response with sheet resistance

To further investigate the improved blue-response, we have determined the correlation between blue response and sheet resistance for D0, D7 and E7, see figure 2. In the standard picture I_{blue} is expected to increase with increasing R_{sheet}, because a large R_{sheet} is associated with a thin emitter. Instead, we find that the blue response decreases with increasing sheet resistance for D0 and D7 while both parameters are uncorrelated for E7. At high phosphorous concentrations (small R_{sheet}), I_{blue} is equal for all three groups and phosphorous gettering of impurities present in the front region can occur (7,8). In emitters with a lower phosphorous concentration (high sheet resistance), the front region of the cells in D0 and D7 is of lower quality than that in E7, where the aluminium presumably takes over the gettering action of phosphorous.

It is still unclear why P and Al act in a complementary fashion. The fact that the sheet resistance increases after an anneal with an aluminium-doped back-side indicates that aluminium either is present as electrically active acceptors or reduces the concentration of electrically active phosphorous by complex-formation with P. To further investigate this, anneals could be performed in presence of aluminium with and without a phosphorous doped emitter. It is found that shunting of the cells does not occur, even though aluminium has diffused all through the entire thickness of the wafer. This shows that although Al may be present at grain boundaries and reduce recombination even close to or even in the emitter, it does not form ohmic paths across the junction.

Gettering or Passivation?

Finally, gettering of impurities into the Al-doped silicon layer may play a role in the effects observed upon

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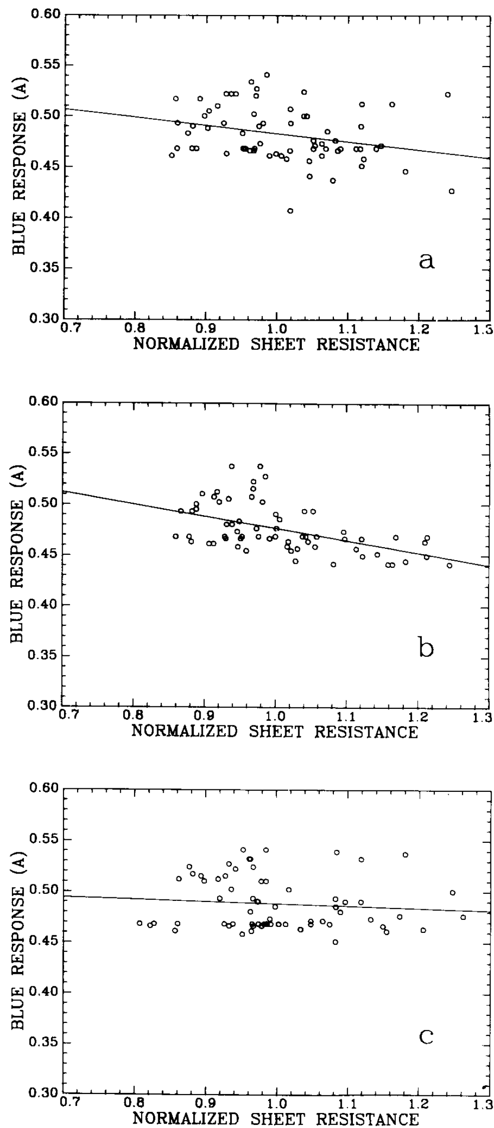

Figure 2. Blue response of groups D0 (a), D7 (b) and E7 (c) versus normalized (with respect to the average) sheet resistance. Solid lines are linear fits to the data. In group D7 (slope = -0.08 ± 0.03 A^{-1}) a significant decrease in I_{blue} is observed for large sheet resistance. I_{blue} in E7 (slope = $-0.02 \pm 0.03 A^{-1}$) is independent on R_{sheet} . D0 shows a slight decrease in I_{blue} with increasing R_{sheet} (slope = -0.12 ± 0.03 A^{-1}).

annealing. The improved quantum efficiency in the blue part of the spectrum in presence of aluminium and the increase in sheet resistance upon annealing suggest that diffusion of Al rather than back-side aluminium gettering occurs. The data presented here comprises anneals for one duration and do not provide insight in the activation energies which play a role. The density of states in the band-gap at the grain boundaries is expected to change upon annealing with a doped back-side. Deep Level Transient Spectroscopy may reveal the nature of this change. Furthermore, gettering is expected to improve intra-grain minority-carrier lifetime, whereas passivation of grain boundaries only affects the grain-boundary recombination rates. Martinuzzi et.al. (2) have found that in polycrystalline samples annealed at 450 °C for 2 hours, the grains were improved, but the grain-boundary recombination velocity remained unchanged, thus supporting the gettering mechanism at these relatively low temperatures. In the higher temperature anneals, aluminium grain-boundary diffusivity is much larger and passivation is likely to occur.

CONCLUSIONS

The main conclusions are the following. First, the average bulk diffusion length in polycrystalline silicon is increased with 15 % by annealing during one hour at a temperature of 700 °C with an aluminium-doped back side. The same treatment without an Al-doped back side results in a 5 % increase in comparison to unannealed cells. Thus the aluminium amounts for 10 % (absolute) of the enhancement. The mechanism behind this effect is suggested to be grain-boundary and sub-grain-boundary diffusion of aluminium. At these boundaries, Al presumably de-activates electrically active traps. Anneals at other temperatures for 1 hour also resulted in improvements of polycrystalline silicon cell bulk quality.

Second, the electrical quality of the emitter region of the cells was improved by annealing with an aluminum-doped back-side, especially at 600 and 700 °C. From the increase of sheet resistivity upon annealing in E7, it is concluded that aluminium diffuses all through the wafer. It was shown that the increase of I_{blue} comes mainly from those wafers which have a high sheet resistance and hence a lower than average phosphorous concentration in the emitter. In emitters with high phosphorous concentration, impurities and defects in the top region of the cell can be gettered or passivated by phosphorous, whereas in emitters with lower phosphorous concentrations , aluminium -if present- may take over this gettering action and thus act complementary to the phosphorous.

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