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IMPROVED SHORT-CIRCUIT CURRENT OF ION-IMPLANTED CRYSTALLINE SILICON SOLAR CELLS

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ABSTRACT

Poly-crystalline silicon solar cells have been prepared by phosphor implantation in combination with pulsed excimer-laser annealing or thermal annealing. From a comparison between the "cold" laser processed cells and the thermally processed cells it is concluded that the base electrical properties are conserved when laser annealing is employed. This results in a short-circuit current which is 4% higher for laser processed cells than for thermally processed cells.

The short-circuit current of shallow p-n junctions, made by ion-implantation and laser annealling of mono-crystalline Si is found to be increased by 10%, if before implantation a thin amorphous Si layer is deposited on the crystal space. This increase is accompanied by an enhanced blue response indicating that the space-charge region is

is accompanied by an enhanced blue response, indicating that the space-charge region is free of implantation-tail damage. The amorphous layer is thought to act as a dechanneling layer for the implanted ions.

1. INTRODUCTION

Ion-implantation and subsequent pulsed laser annealing (PLA)^{1.5} is proven to be a promising technique for the p-n junction processing of crystalline silicon solar cells. The advantage over conventional furnace diffusion and annealing techniques is that shallow, high-quality junctions with a well-controlled junction profile can be processed. Moreover, bulk electrical properties can be maintained because of the "cold" processing. This is especially of importance now that poly-crystalline silicon (poly-Si) has become an attractive alternative to mono-crystalline Si (mono-Si) as a base material. Using poly-Si it is possible to achieve a noticeable reduction in cell price⁶. However, standard furnace diffusion and annealing techniques are not optimal prices. However, standard furnace diffusion and annealing techniques are not optimal for processing poly-Si because the material is very sensitive to high-temperature processes which can degrade the electrical quality⁶⁻¹¹. Thus, to improve the efficiencies of poly-Si solar cells, development of a "cold" process is important. Also for processing of lower-purity "solar grade" Si¹², which might become available in future as a cheaper alternative for the commonly used poly-Si, such a process is needed.

Ion-implantation is now an established high-throughput process. In a standard high-current low-energy (10-20 keV) implanter all dopants can be introduced in a wafer in typically a few seconds. During implantation the wafers remain at room-

temperature. Due to the implantation a top-layer with a thickness in the order of several tens of nanometers is amorphized. To activate the dopants in this layer, laser annealing can be employed. Using this process only the top micrometer of the material is heated considerably above room-temperature. Recently high repetition-rate excimer-lasers have become available for large-area annealing. Annealing of a complete wafer can now be done in a time in the order of seconds to a minute. Because of the low processing temperatures of both processes mentioned, their combination is of great

Using ion-implantation and laser annealing to produce high-efficiency cells on Using ion-implantation and laser annealing to produce high-efficiency cells on mono-Si, the following problem arises: Before the top layer of the crystal is amorphized, the implanted ions can channel into the crystal, giving rise to relatively deep defects ¹³. Especially when low laser energy-densities are used in order to create shallow junctions, these defects are not annealed. Thus they cause a degradation of the crystal quality exactly in the sensitive space-charge region⁵. Although mis-aligning the crystal during implantation gives some improvement¹⁴, a lot could be gained if this channeling effect is completely avoided. One way to do this employs an amorphous layer which is deposited on the crystal prior to implantation. All implanted ions are stopped in which is deposited on the crystal prior to implantation. All implanted ions are stopped in the top-layer, and channeling is prevented. The underlying crystal remains free of defects, and an anneal with a low laser energy-density suffices to obtain shallow junctions with an improved blue response.

In this paper we present a comparison between excimer laser- and thermal annealing for ion-implanted poly-Si solar cells in order to demonstrate the importance of "cold" processing. Further we investigate the effect of the use of a dechanneling layer in the processing of ion-implanted mono-Si solar cells.

2. COMPARISON BETWEEN EXCIMER LASER- AND THERMAL ANNEALING

2.1. Experimental

5x5 cm² cast poly-Si Wacker SILSO wafers, doped p-type to a concentration of 10¹⁶ cm⁻³ were selected. All wafers were neighbours from one part of an ingot. In this way the natural spread in cell parameters due to differences in grain structure and diffusion length was minimized. No mechanical polishing was applied. The surface damage due to the wafer sawing was removed by means of an HF/HNO₃/CH₃COOH (2:7:2) etch. 40 µm was removed from each side of the 400 µm thick wafers.

The frontside of all wafers was implanted at room-temperature up to a dose of 3x10¹⁵ cm⁻² with 10 keV P⁺. The backside was implanted up to a dose of 3x10¹⁵ cm⁻² with 20 keV B⁺ to form a degenerate p⁺ layer. During implantation a 1 mm wide strip near the edges was masked to avoid short-circuiting of the completed cells.

After implantation the wafers were divided into two sets. The front and backside of wafers of the first set (¬PI A¬) were annealed in air at room temperature using a pulsed

wafers of the first set ("PLA") were annealed in air at room temperature using a pulsed excimer-laser (FWHM = 25 ns, λ = 308 nm) with an energy-density of 1.2 J/cm^2 . To obtain the proper energy-density over the whole area, the 4x18 mm² size laser beam (containing 120 mJ) was focussed and scanned over the wafer using a two-axis mirror scanner. Pulse overlap was at least 50%. The laser being operated at a repetition rate of

25 Hz, annealing of one side of a wafer could be performed within 2 minutes.

The wafers of the second set ("TA") were thermally annealed in a vacuum furnace.

The anneal consisted of two steps: 30 min at 600 °C, followed by 15 min at 900 °C. The heating rate was 1 °C/s, the cooling rate 0.25 °C/s.

After p-n junction processing, electron-beam evaporated Ti/Pd/Ag grids with a

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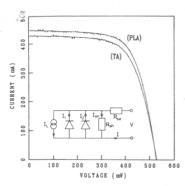


Figure 1
Typical measured currentvoltage characteristics of cells
processed by ion-implantation
and subsequent laser annealing
(PLA) or thermal annealing in
vacuum (TA). In addition,
results from curve-fitting
according to the two-diodes
shown as an inset are shown.
Fitting parameters are given in
Table I.

| | | TA | PLA | |
|--|---|---|--|--|
| Isc Ired Iblue FF Rse Rsh | (mV) (mA) (mA) (mA) (%) (%) (μΩ) (Ω) (pA/cm ²) (μA/cm ²) (mA/cm ²) (cm ²) | 530. 437. 234. 113. 65. 6.5 117. 30. 10.4 0.30 19.1 23.0 | 530. 453. 250. 115. 68. 7.1 92. 48. 10.9 0.31 19.7 23.0 | (open-circuit voltage) (short-circuit current) (short-circuit current, AM1 filtered for λ>600 nm) (short-circuit current, AM1 filtered for λ<600 nm) (fill-factor) (efficiency) (series-resistance) (shunt-resistance) (saturation current-density diode 1) (saturation current-density diode 2) (light-generated current-density) (active area) |

Table I. Averaged measured and calculated electrical parameters of solar cells processed using ion-implantation in combination with thermal annealing (TA) or pulsed-laser annealing (PLA)

coverage of 10% (optimized for an emitter sheet resistivity of 30 Ω /square) were applied on all wafers. The contacts were sintered after evaporation for 10 min at 400 °C to obtain ohmic contacts.

°C to obtain ohmic contacts. Cell performance was measured at 25 °C under 1000 W/m² AM1 illumination. Additional information about the electrical processes within the cells was obtained by applying a curve-fitting procedure to the measured I(V) curves 15 . This was done on the basis of a two-diodes model also containing series- and shunt-losses 15 . Spectral response measurements were done using blue and red filters ($\lambda <$ > 600 nm).

2.2. Results and Discussion

Fig. 1 shows measured I(V) characteristics of two typical cells prepared on two

neighbouring wafers using the different methods of junction preparation as described above. The full drawn lines represent computer-fits according to the two-diodes model shown as an inset in the figure. The measured electrical parameters and the obtained fit-parameters are given for both cells in Table I.

fit-parameters are given for both cells in Table I.

The open-circuit voltages obtained on cells of type PLA are equal to those obtained on cells of type TA. This indicates that the behaviour of a junction processed by ion-implantation and pulsed-laser annealing is very similar to that of a junction made by ion-implantation and thermal annealing. This is also illustrated by the results from curve-fitting. The diode saturation currents J₀₁ and J₀₂ are nearly equal for both types of cells. However, the short-circuit current of the PLA cells is 4% higher than that of the TA cells. This is mainly caused by a difference in the long-wavelength response (I_{red}), as can be seen in Table I. The long-wavelength response is determined by electrical processes in the base regions of the cells. As far as the base region is concerned, the only difference between laser annealing and thermal annealing is the temperature during processing. Apparently the minority-carrier diffusion length in the base region is decreased upon annealing at 900 °C6,7. This diffusion length in the base region and oxygen impurities from the crucible in which the material is cast, intrinsic (metallic) impurities or structural defects might play a role. As the nature of these defects and impurities is very complex, it is not well possible to attribute the found decrease in diffusion length to specific recombination processes. Whatever the exact mechanisms might be, it is evident that for this material the high-temperature processing employed here results in the formation or activation of recombination centers.

3. IMPROVED BLUE RESPONSE BY IMPLANTATION INTO DECHANNELING LAYERS

3.1 Experimental

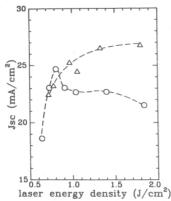
Two sets of 8x8 mm² solar cells were prepared on polished single-crystal <100-silicon, on one set of which 500 Å amorphous silicon was deposited. This deposition was performed under UHV conditions after the front surface was made atomically clean. Both sets were implanted with 3x10¹⁵ cm², 10 keV P+(front) and 2x10¹⁵ cm², 20 keV B+(back). During implantation the wafers were tilted over an angle of 7°, a commonly used method¹⁴ to avoid excessive channeling. Implantation damage was annealed using a scanning pulsed ruby laser (fwhm=32 ns, \lambda=694 nm) with a guide diffuser (using this laser the threshold for epitaxial regrowth is 0.85 J/cm² for both types of samples). Following laser annealing the cells were heated to 450 °C during 10 minutes to remove quenched-in defects¹6. After a dip in 10% HF, Ti/Pd/Ag contacts were evaporated and sintered for 10 minutes at 350 °C. No AR coating was applied, and no attempt was made to passivate the surface.

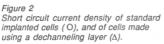
Cell performance was measured at 25 °C under 1000 W/m² AM1 illumination. Spectral response measurements were done using blue and red filters (λ </> <00 nm).

3.2 Results and Discussion

The short-circuit current-density as function of laser energy-density of both sets of cells is shown in Fig. 2. The control set reproduces earlier results on implanted mono-Si 5 , showing a decrease of J $_{\rm SC}$ as the laser energy-density increases from 0.9 to

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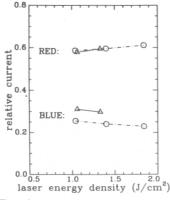


Figure 3 Red and Blue contributions to J_{SC} of some control cells (O), and of cells made using a dechanneling layer (Δ).

2.0 $\rm J/cm^2$. This can be explained by pointing out that as the laser energy-density increases, so do the melt- and junction depth. Thus the blue response of the cell decreases. In the same energy-density range, $\rm J_{sc}$ of the set of cells made using a dechanneling layer is improved with up to 10 %, compared to $\rm J_{sc}$ of the control set. The increase of $\rm J_{sc}$ with the laser energy-density in spite of the increased junction depth is probably caused by contaminants in the deposited layer, which lose importance as the thickness of the emitter increases. An indication for the presence of these contaminants

(e.g. H_2O , H_2 , O_2 which are known to diffuse into the amorphous layer upon exposure to air) is the low value of V_{oc} that was found for the novel cells. In Fig. 3 the relative contributions of red and blue response to J_{sc} are shown, and it can easily be seen that the increase in J_{sc} for the novel cells is due to an increase in the blue response. This indicates that in spite of contamination of the emitter, the quality of the shallower regions (< 2 μ m) of cells processed using dechanneling layers in superstant to the first traditionally impossible declaration. is superior to that of traditionally implanted cells

4. CONCLUSIONS

Wacker SILSO poly-Si cells made by phosphor implantation and pulsed excimerwacker sits of poly-si cells made by phosphor implantation and pulsed exciner-laser annealing of smooth acid-etched base material yield a short-circuit current which is typically 4% higher than that of cells made by phosphor implantation and thermal annealing in vacuum at a maximum temperature of 900 °C. This difference originates from a degradation of the minority-carrier diffusion length in the base region of the cells due to the high-temperature thermal annealing resulting in activation or formation of recombination centers. Thus, the advantage of the "cold" laser annealing process in combination with ion-implantation is proven. The difference in diffusion length can partly be related to intrinsic impurities. In that case the temperature effect is expected to become more pronounced when, in future, solar grade base material will be used.

Shallow junctions of high quality can be made on crystalline substrates using low-energy ion-implantation into a deposited layer of 500 Å amorphous Si. Solar cells made using this technique show a short-circuit current increase of 10 % relative to cells made by standard ion-implantation. This improvement is due to an enhanced blue response and probably originates from the absence of implantation tail damage in the space-charge region.

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REFERENCES

- R.T. Young, R.F. Wood and W.H. Christie, J. Appl. Phys. 53 (1982) 1178
- R.T. Toung, R.F. Wood, J. Narayan, C.W. White and W.H. Christie, IEEE Trans. Electron. Dev. **ED-27** (1980) 807
- Dev. ED-27 (1980) 807

 D.H. Lowdnes, J.W. Cleland, W.H. Christe, R.E. Eby, G.E. Jellison, J. Narayan, R.D. Westbrook, R.F. Wood, J.A. Nilson and S.C. Dass, Appl. Phys. Lett. 41 (1982) 938

 G.G. Bentini, R.Galloni, R. Rizzoli, C. Summonte, Q. Zini, F. Zignani, Proc. 6th E.C. Photovoltaic Solar Energy Conf. (1985) 990, editors: W. Palz and F. C. Treble, Reidel Publ. Comp., Dordrecht, Holland

 W. Sinke, A. Polman, W.G.J.H.M. vah Sark and F.W. Saris, Proc. 6th E.C. Photovoltaic Solar Energy Conf. (1985) 1095, editors: W. Palz and F. C. Treble, Reidel Publ. Comp.,
- 5) Dordrecht, Holland E. Fabre, Proc. 4th E.C. Photovoltaic Solar Energy Conf. (1982) 346, editors: W.H. Bloss
- 6)
- E. Fabre, Proc. 4¹¹ E.C. Photovoltaic Solar Energy Conf. (1982) 346, editors: W.H. Bloss and G. Grassi, Reidel Publ. Comp., Dordrecht, Holland C.T. Ho and F.V. Wald, Phys. Stat. Sol. (a) 67 (1981) 103

 M.B. Spitzer, C.J. Keavney, R.G. Wolfson and R.J. Matson, Proc. 17th Photovoltaic Specialists' Conf., Kissimee, FL, 1984, IEEE, New York, 252

 D. Redfield, Appl. Phys. Lett. 38 (1981) 174

 L.L. Kazmerski, Proc. 5th E.C. Photovoltaic Solar Energy Conf. (1984) 40, editors: W. Palz and F. Fittipaldi, Reidel Publ. Comp., Dordrecht, Holland
- 10)

- Patz and F. Fittipaldi, Reidel Publ. Comp., Dordrecht, Holland G.B. Turner, D. Tarrant, D. Aldrich, R. Pressley and R. Press, Proc. 16th Photovoltaic Specialists' Conf., San Diego, CA, 1982, IEEE, New York, 775
 H.A. Aulich, Proc. 5th E.C. Photovoltaic Solar Energy Conf. (1984) 936, editors: W. Palz and F. Fittipaldi, Reidel Publ. Comp., Dordrecht, Holland P. Blood, G. Dearnaley and M. A. Wilkins, Rad. Eff. 21(1974) 245
 K. Cho, W. R. Allen, T. G. Finstad, W. K. Chu, J. Liu and J. J. Wortman, Nucl. Instr. & Meth. B7/8 (1985) 265 14)
- A. Polman, W.G.J.H.M. van Sark, W. Sinke and F.W. Saris, Solar Cells 17 (1986) 241 A. Mesli, J.C. Muller, D. Salles and P. Siffert, Appl. Phys. Lett. 39 (1981) 159