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Polyx multicrystalline silicon solar cells processed by PF_5^+ unanalysed ion implantation and rapid thermal annealing

W. O. Adekoya, Li Jin Chai (*), M. Ajaka, J. C. Muller and P. Siffert

CRN (IN2P3), Laboratoire PHASE (UA du CNRS n° 292), 23, rue du Loess, 67037 Strasbourg Cedex, France

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Résumé. — Le recuit transitoire des défauts induits dans le silicium par l'implantation d'ions peut être une technique compétitive par rapport au recuit classique pour la fabrication des photopiles à usage terrestre. Il reste cependant quelques inconvénients, tels qu'une faible durée de vie des porteurs photogénérés et une tension en circuit ouvert peu élevée. Nous avons tenté de surmonter ces difficultés pour le silicium multicristallin (POLYX) produit par la CGE (France) en choisissant une température de recuit de la jonction dopée au phosphore, d'une part, assez élevée, 800 °C (afin d'obtenir une bonne recristallisation et une activation suffisante du dopant) et d'autre part, suffisamment faible, 900 °C (afin de réduire les effets de dégradation des propriétés électriques de la base). Le but de ce travail est d'étudier les caractéristiques *I-V* des photopiles et de les comparer à celles obtenues par recuit classique ou par diffusion du dopant.

Abstract. — Rapid thermal annealing of damage induced by implantation in silicon can be a cost effective technology for the processing of terrestrial solar cells as compared to classical furnace or pulsed laser annealing. Unfortunately, drawbacks as poor bulk lifetime or low open-circuit-voltage occur as well. We have attempted to overcome these limitations for POLYX multicrystalline cast silicon grown by CGE (France) by keeping the annealing temperature of the phosphorus doped layer as high as 800 °C (to ensure a good crystalline quality and a high dopant activation) while being less than 900 °C (to minimize the effect of degradation of the base properties). The purpose of the present work is to investigate the *I-V* characteristics of the cells and to compare to those obtained with classical furnace annealing or with classical diffusion process.

1. Introduction.

Multicrystalline silicon can be considered as an attractive alternative to single crystal silicon as base material for the fabrication of solar cells. It offers the possibility of achieving strong reduction of cell cost in spite of a relatively small decrease in efficiency. Parallel to the work on new crystal growth methods including ribbon sheet, pulling and cast ingot growing, the increasing use of « off grade » low cost silicon necessitates the optimization of the cell manufacturing process and especially the junction formation. During the last ten years, ion implantation has gained acceptance as a highly effective junction formation process. The results of several studies indicates that excellent solar cells can be fabricated [1, 2], and the ion implantation process has been applied to the fabrication of space [3], flat plate [4], concentrator [5] and high efficiency [6] solar cells, with notable performances achieved for each type of cell. Nevertheless the high cost of conventional ion implanters has prevented widespread use of implantation for solar cell manufacture, so that, alternative procedures using unanalysed ion implantation [7, 8], or glow discharge [9] have been proposed.

In the case of large grains multicrystalline silicon solar cells, realised by ion implantation, only few studies are reported in literature : phosphorus and arsenic implantation followed by incoherent light annealing [10, 11] ; PF_5 glow discharge plus UV laser annealing [12], PF_5 unanalysed implantation + YAG and CO_2 laser annealing [13, 15].

In this work, we propose for POLYX material the realization of shallow N^+ P junction by coupling an unanalysed ion implantation procedure with a rapid thermal annealing processing. Fast dopant activation

(*) On leave from the lab. of Ion-beam Physics, Wuhan Univ. Wuhan (China) as well as negligible redistribution are the two essential advantages of this annealing procedure. But the two major problems, which are the reduction of the minority carrier lifetime in the bulk and the presence of residual defects in the space charge as well as in the front region, imply serious limitations to the process as the open-circuit voltage and the quantum efficiency are affected. We have therefore attempted to overcome these limitations in multicrystalline silicon solar cells through keeping the annealing temperature in the range of 800 to 900 °C. The results of experiments carried out on devices from POLYX (CGE) material with implanted N^+ P junctions are presented. The electrical properties were analysed by using sheet resistance measurements, dark and AMI illumination *I-V* characteristics, as well as spectral response. Our choice of annealing parameters was based on results from studies carried out on single crystal silicon of a similar resistivity as the wafer used in this work. Various analysis like Rutherford Backscattering (RBS), Transmission Electron Microscopy (TEM), Sheet resistance, carrier concentration and mobility profiling, and Deep Level Transient Spectroscopy (DLTS) measurements, all show that an annealing temperature range of 800-850 °C for 4-5 s, appears to be optimal for our experimental conditions.

2. Experimental conditions.

2.1 DOPING. — As industrial necessity of high production rates over large surface wafers results in using sophisticated and expensive ion implantation equipment, we have proposed the realization of solar cells by using a low cost, high current, low energy, unanalysed ion implantation procedure [7], which needs no sophisticated magnetic network for isotope selection, nor long beam lines. This doping processing has been called AMI (Atomic and Molecular ion Implantation). Phosphorus ions were implanted at 30 keV energy by using this technique at an optimized dose of 2-3 × 10^{15} ion/cm^2. The uniformity is about 10 % accross the wafer and 10 % wafer to wafer as determined by means of the four points probe technique performed after annealing.

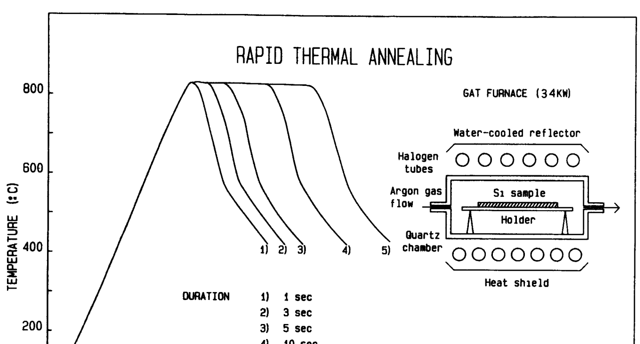

Fig. 1. — Schema of the Rapid Thermal Annealing (RTA) set up together with the microprocessor controlled thermal cycle.

2.2 ANNEALING. — The system of Rapid Thermal Annealing (RTA) used here is a commercially available furnace (34 kW power HEATPULSE machine [16]) with a compressed air and water cooled reflector to ensure a good temperature homogeneity of the sample holder. A continuous high purity argon gas flow is maintained through the chamber during the whole annealing process. The temperature is controlled by an optical pyrometer connected to a microprocessor. The heating rate is fixed at about 50 °C/s and the cooling rate is about 100 °C/s (see figure 1). In order to compare the RTA annealing to the classical one, 10 cm^2 POLYX slices from the same ingot (n° 633, resistivity 1.96 Ω.cm) were cut in 2 cm^2 samples, so that there were many samples for each slice number. For the electrical analysis, we have restricted our study to two slices (number 33 and 43) coming from the middle of the ingot. The measurements were performed on 3-4 samples for each experimental condition, so that the maximum scattering of the results, were taken in consideration.

2.3 CELL PROCESSING. — The contacts of the cells were obtained by simple vacuum evaporation of a Au layer on the back, while a Ag grid covers about 12.5 % of the front surface. The cells were tested on a simulator adjusted to deliver 100 mW/cm^2 (AMI conditions). The measurements were taken at 28 °C.

3. Characteristics of the doped layer.

3.1 REGROWTH BEHAVIOUR. — We report in figure 2 the RBS spectra obtained for ⟨100⟩ monocrystalline silicon samples annealed at 615, 725, 770, 820 and 980 °C for 4 s. The comparison between the aligned and the random curves shows that within the temperature range 615-770 °C, the damaged layer is still amorphous while an annealing at 820 °C is sufficient to have a crystal quality close to that of a virgin sample as confirmed by measuring the minimum yield χ_{min} which reaches a value of 5 %.

Complementary Transmission Electron Microscopy (TEM) [17] measurements confirm the relative good crystal quality for 820 °C/4 s annealing with only the presence of small 100-200 Å diameter defects, probably precipitates ; whereas at temperatures above 950 °C dislocation loops and rod-shaped defects appears.

3.2 DLTS ANALYSIS. — Since our RBS and TEM data indicate that 820 °C/4 s appears to be the best

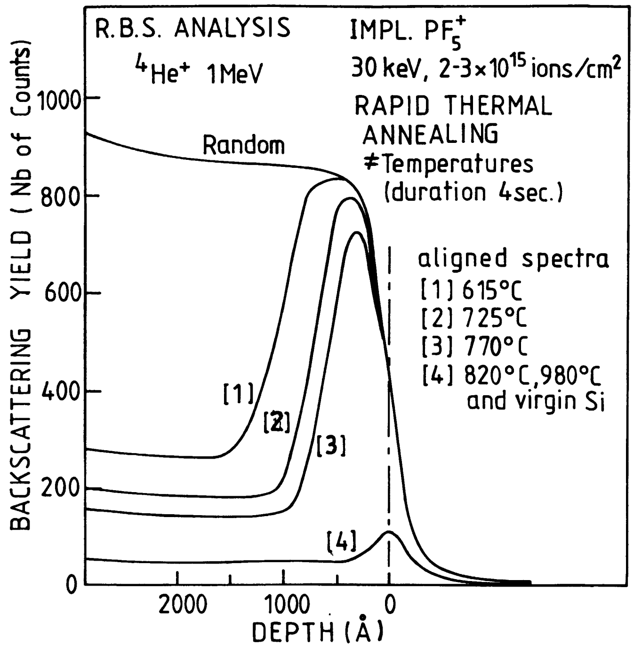

Fig. 2. — Rutherford Backscattering (RBS) measurements of the residual disorder after RTA process.

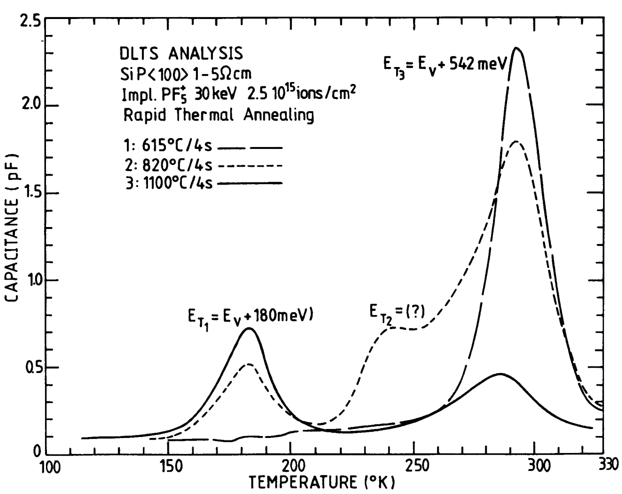

Fig. 3. — DLTS signal for a PF_5^+ implanted sample annealed at 615 °C/4 s, 820 °C/4 s and 1 100 °C/4 s.

temperature/time compromise in order to achieve good crystal quality, we have investigated, using the DLTS technique, a series of samples annealed under these conditions as well as above and below it in order to see the evolution of electrically active defects within the range 600-1 100 °C. Our main results are summarized in figure 3.

These results indicate that one defect level at 542 meV with a concentration and effective cross section of $2.7 \times 10^{14}\ cm^{-3}$ and $2.1 \times 10^{-14}\ cm^{-2}$, respectively had formed at 615 °C/4 s. This same level was observed in all the other samples annealed up to 1 100 °C/4 s, we remark that its concentration greatly diminished at the highest temperature.

At 820 °C/4 s, two other levels are seen to have formed one of which is not yet characterizable. The other level shows up at 180 meV with a concentration of $4.8 \times 10^{13}\ cm^{-3}$ and an effective cross-section $9.3 \times 10^{-16}\ cm^2$. This level was again observed after 1 100 °C/4 s annealing, however, with a higher concentration as shown in figure 3.

The kinetics of formation of these levels is the subject of another study, but their importance at the moment is seen in the fact that under quasi-ideal annealing conditions, they remain in the junction.

3.3 ELECTRICAL PROPERTIES. — In figure 4, the sheet resistance of the N^+ doped layer of POLYX multicrystalline silicon is plotted a) *versus* the annealing temperature in the range 700-1 000 °C for a 4 s duration, b) *versus* annealing time for a temperature of 850 °C. It is noteworthy that the sheet resistance reaches a minimum value of 90-110 Ω/□ when the annealing temperature is more than 800 °C. This value is as low as those obtained for the classical thermal process (three-step annealing 550 °C, 1 h ; 850 °C, 1/4 h ; 550 °C, 1 h) (Fig. 4c).

Moreover, it is known that to avoid degradation effects on the lifetime of minority carriers in the bulk, it is necessary to utilize the lowest annealing temperature which gives a good recrystallization of the amorphized layer. For this reason, we decided to carefully analyse the 800-900 °C range for annealing times between 2 and 8 s.

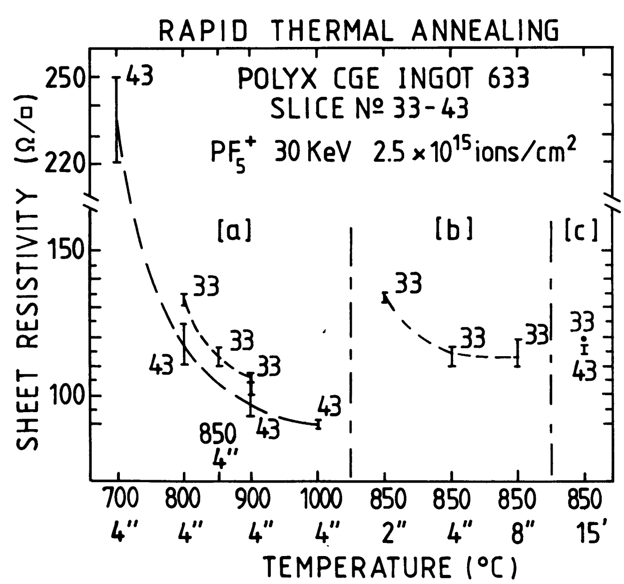

Fig. 4. — Evolution of the sheet resistance as a) a function of RTA temperature for 4 s heating time, b) a function of processing time for a temperature of 850 °C, c) as obtained for a three-step annealing (550 °C, 1 h ; 850 °C, 1/4 h, 550 °C, 1 h).

In figure 5, we have reported the carrier concentration profiles as deduced from anodic stripping technique for ⟨100⟩ monocrystalline silicon samples annealed at different temperature-time couples, which give a maximum activation of the dopant. The phosphorus peak activity reaches a level close to the equilibrium solubility limit (about 4×10^{20} cm^{-3}) for temperature-time couples such as (75 °C, 15 s) or (900 °C, 2 s). The phosphorus active fraction, as deduced from the total incident dose of the $\sum_{0<n<5} PF_n$ ions is about 24 % to 30 %. It is also to be noted that no diffusion occurs by increasing the temperature due to shorter processing durations.

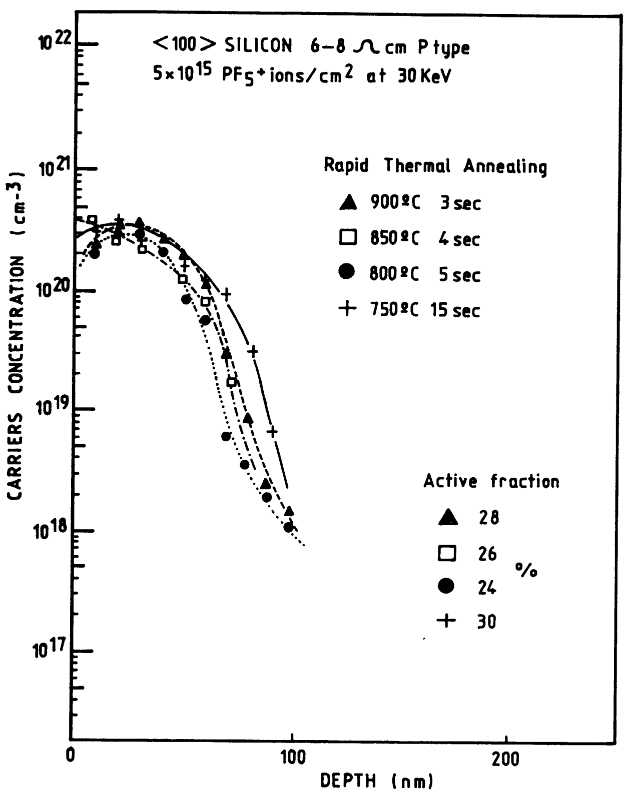

Fig. 5. — Carrier concentration profiles of ⟨100⟩ monocrystalline silicon samples annealed at different RTA temperature-time couples.

4. Photovoltaic performances.

In table I, we present a comparison of the results of the AMI performance of the single crystal and polycrystalline cells. Our results for the former are compared with those obtained from cells prepared by implantation of P^+ and PF_5^+ ions followed by a similar incoherent light annealing [18] or by liquid phase laser annealing [12-14] and with those reported for SILSO material [10-12].

In the case of single crystal cells, we observed that the short circuit current (I_{sc}) is almost equivalent in all the processed cells, whereas the open circuit voltage (V_{oc}) of the PF_5^+ implanted samples is low (below 500 mV) when compared with results obtained for P^+ implantation [18] and for PF_5^+ after laser annealing [12-14]. This is also the case with the polycrystalline cells. These low V_{oc} values can be attributed to the persistence of a defective region near the junction as confirmed by DLTS and also to the presence of fluorine which inhibits the regrowth during annealing [17, 19]. The results from the cells

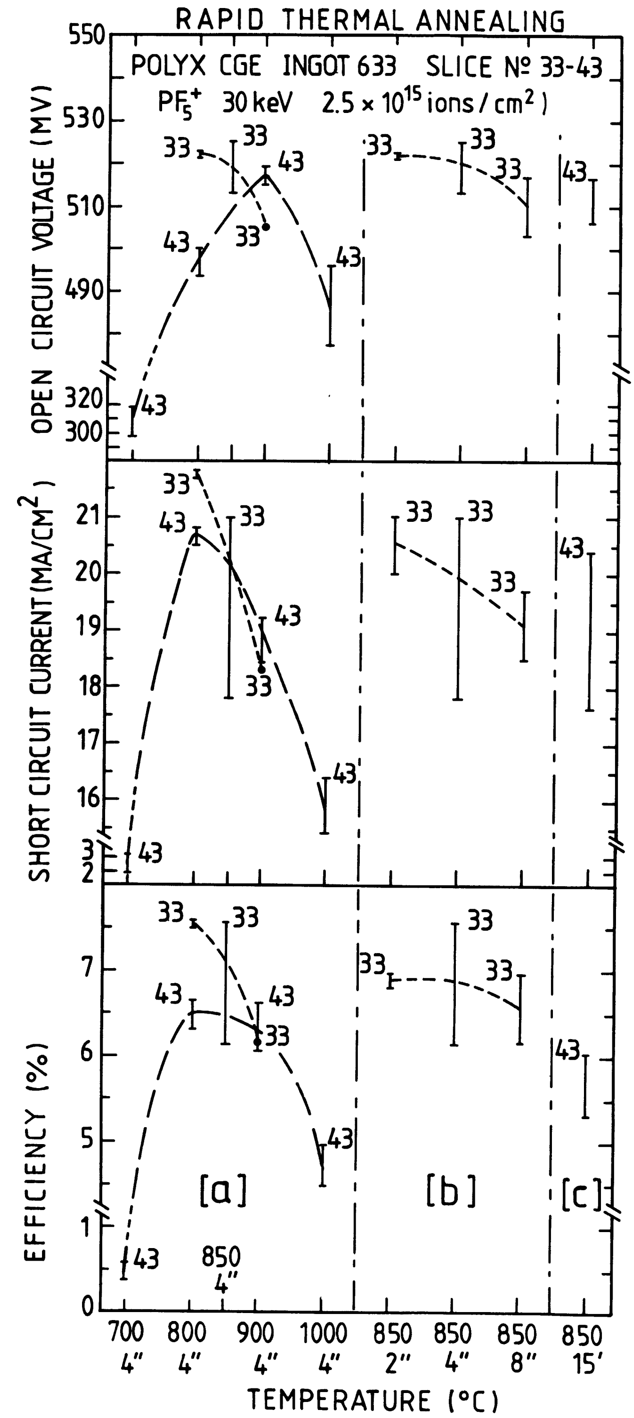

Fig. 6. — Evolution of the V_{oc}, I_{sc} and η as a function of RTA : a) temperature and b) duration ; c) classical three-step annealing for POLYX 2 cm^2 cells.

processed on the POLYX ingot 633 using the RTA annealing set-up are compared with those from cells prepared using the classical three-step annealing procedure (i.e. 550 °C, 1 ; 850 °C, 1/4 h ; 550 °C, 1 h).

For the purpose of comparison, we show in figure 6 the evolution of the open circuit voltage (V_{oc}), the short circuit current (I_{sc}) and the efficiency (η) for the fast thermal processing a) in the temperature range 700-1 000 °C for a fixed annealing time 4 s, b) at a fixed temperature 850 °C for different times, and c) for the classically annealed reference samples. For these series of measurements performed on POLYX material, we have a large scattering in the experimental results more especially for the I_{sc} current and for efficiency values (about ± 10 %) than for the sheet resistance and the V_{oc} values. This scattering effect is in agreement with other results obtained on SILSO material for a similar annealing technique [10, 11].

One can see on this figure :

— that the V_{oc} values in the range 800-900 °C are as good as the values reported for classical annealing and that the annealing duration plays a negligible role in this case ;

— that higher current values than those obtained for the three-step process can be obtained for the lower annealing temperature of 800 °C which from RBS results, assures a sufficient regrowth of the damaged layer. However, the annealing duration is important here as the I_{sc} values decrease as a function of increasing the duration in the range 2-8 s ;

— finally, the efficiency values confirm these tendencies so that the rapid thermal processed cells have about one per cent more conversion efficiency than those obtained from the three-step annealing.

However, the results obtained to date by the association of the Rapid Thermal Annealing (RTA) with the Atomic and Molecular ion Implantation (AMI) have not reached the level of those processed using for doping, classical ion implantation or diffusion of the dopant, and pulsed laser for the annealing (see Table I).

5. Conclusion.

The aim of this study was the investigation of the possibilities offered by the Rapid Thermal Annealing (RTA) to regrow the POLYX silicon damaged layer due to the doping process using the Atomic and

Table I. — *Photovoltaic properties of mono and polycristalline cells produced by* AMI *implantation followed by classical and* RTA *annealing. Some results, obtained by classical ion implantation or by classical diffusion of the phosphorus dopant are given for comparison.*

Doping	Annealing	Material	V_{oc}	J_{sc} (mA/cm^2)	*FF*	(%)	Réf.
PF_5 30 keV 3 × 10^{15} ions/cm^2	RTA furnace 820 °C, 10 s	Si mono	490	22.5	0.68	7.5	[18]
PF_5 30 keV 2 × 10^{15} ions/cm^2	Scanned Incoherent Light	⟨ 100 ⟩	492	22.7	0.75	8.4	
p^+, 10 + 40 keV 2 × 10^{15} ions/cm^2	Scanned Incoherent Light	1.5 Ωcm	560	24.2	0.70	10.0	
PF_5 30 keV 2-3 × 10^{15} ions/cm^2	RTA furnace 800 °C, 4 s	Si poly	519	21.7	0.66	7.5	Present work
PF_5 30 keV 2-3 × 10^{15} ions/cm^2	Classical furnace 850 °C, 15 min	POLYX ingot 633	514	20.4	0.58	6.0	
Phosphorus diffusion	—	2 Ωcm	566	20.5	0.72	8.44	[20]
P^+, As^+	Incoherent light	Si poly SILSO	470 to 490	—	—	5.8 to 7.0	[10, 11]
PF_5 2 KeV	Pulsed U.V. laser	SILSO	560	21.6	0.76	9.3	[12]
PF_5^+ 10 KeV	Pulsed YAG laser	POLYX	567	29.2 (*)	0.63	10.4 (*)	[13, 14]

Cells tested under AM1 conditions with (*) or without anti-reflective coating.

Molecular ion Implantation (AMI) process with PF_5^+ ions.

Our main results show that cells have not reached in the present processing conditions, the level of cells processed with the conventional technique, even though the regrowth and electrical activation seem to be sufficient. The V_{oc} and efficiency limiting factor which result from this processing is due to residual defects and to the presence of fluorine. A better controled and possibly slower cooling rate can be the way to eliminate this serious drawbacks.

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