Plasma Immersion Ion Implantation applied to P+N junction solar cells

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Abstract: Plasma immersion ion implantation is an alternative doping technique for the formation of Ultra Shallow Junctions in semiconductor. In this study, we present the PIII technology developed by the company Ion Beam Services and called PULSION®. We explain the advantages of PIII for the conception of thin emitter solar cells and the use of N type silicon in the fabrication of photodiode. Electrical characterisations of solar cells prepared by immersion of silicon wafer in BF_3 plasma are presented, showing a satisfying photovoltaic behaviour and more specially an increase of internal quantum efficiency in the short wavelength range, due to the thickness of the emitter.

Keyword: Plasma immersion ion implantation, shallow junction, N-type Silicon, Solar cells.
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INTRODUCTION

Among different existing doping techniques, beam line implanter has a predominant place in semiconductor's industry. But due to the decrease of transistor size and so the decrease of source/drain extension, new ways of doping techniques are being studied, among them Plasma immersion ion implantation offers possibility to reach ultra low acceleration energies [2-7]. A PIII prototype called PULSION®, developed by Ion Beam Services Company, is described in Fig.1. [8-9]

The PIII technique is constituted by a vacuum chamber containing a chuck, a plasma source and a power supply.
A specific voltage permits the formation of a sheath around the wafer. Then, doping ions are projected on the sample and implanted in the material at depth varying from some nm to several hundreds of nm.
This process allows a high dose implantation of doping species during a short time, which promises to be interesting for low cost solar cells. Moreover, this technique gives the advantage of processing a large area and ensuring a great productivity.

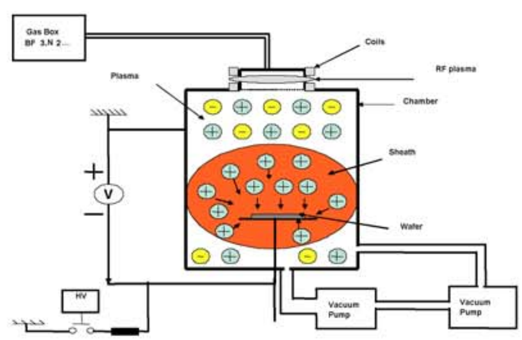

FIGURE.1: Schema of Plasma immersion ion implanter

Time-of-Flight Secondary Ion Mass Spectrometry (ToFSIMS) measurements have been realised in order to analyse the metallic contaminations. Fig.2 presents the level of contamination for Plasma immersion ion implantation by PULSION® in comparison with the limits given by ITRS2005. Even if Ni and Cu concentrations are slightly high for PULSION®, the global contamination level remains acceptable for semiconductor applications like solar cells.

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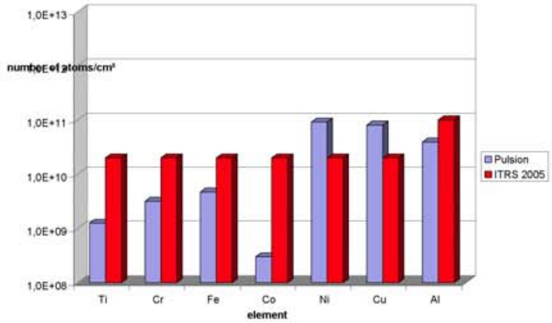

Fig.2: ToFSIMS Measurements: Metallic contaminations

Why N-type for Photovoltaic industry?

Former studies of ultra shallow junctions in N-type silicon with BF_3 PIII convinced us to study the fabrication of P-type shallow emitter photodiodes.
In a previous work [10], a comparison between N^+PP^+ and P^+NN^+ solar cell structures was elaborated by means of PC1D4 software simulations.

The simulated internal quantum efficiency of solar cells revealed to be 1% higher with P^+NN^+ structures.
Besides, the simulations pointed out the reduction of emitter depth results in an increase of sensitivity in the blue range.

From a material point of view, in P-type (boron-doped silicon) the boron-oxygen complexes formed after a prolonged exposure of solar cells become minority carrier recombination centers.
This problem is avoided with the use of N-Type phosphorous-doped silicon.
S.Martinuzzi and al. have demonstrated that in N-type silicon the capture cross sections of metallic impurities are neatly smaller than in P-type [11]. Table 1 illustrates this matter.

Impurity	E_t (eV)	S_n (cm^{-2}) P-TYPE	S_p (cm^{-2}) N-TYPE
Fe_i	+ 0.38	$5\ 10^{-14}$	$7\ 10^{-17}$
Ti_i	+ 0.27	10^{-14}	$3\ 10^{-17}$
Mo_i	+ 0.28	$1.6\ 10^{-14}$	$6\ 10^{-16}$
Cr_i	- 0.22	$2\ 10^{-13}$	$8\ 10^{-14}$
Mn_i	+ 0.27	$3\ 10^{-15}$	$2\ 10^{-18}$
V_i	+ 0.2	10^{-16}	$2\ 10^{-18}$
Co_s	+ 0.41	$2\ 10^{-15}$	$5\ 10^{-18}$

Table 1: Capture cross sections of electrons and holes for some metallic impurities

Besides, there is about $2\ 10^6$ kg/year of N-type wastes which could be used for low cost solar cells.
The goal of this work is to demonstrate the interest of solar cells based on thin and highly B-doped emitter. Their sensitivity to short wavelengths prove that such cells can be used for space applications.

EXPERIMENTAL

All the wafers used in this study are N-type Cz (100) and N-type poly-crystalline silicon substrates with a resistivity of 5-10 ohm.cm. First, a LYDOP diffusion of $POCl_3$ during 20 minutes at 850°C on the back side of the wafers is realised in order to optimise the ohmic contact. The emitter is created by BF_3 PULSION® process: three different acceleration voltage are compared (1, 5 and 10 kV) as well as two doses (5e15 and 1e16 at/cm²). Boron is activated by an annealing at 900°C during 30 minutes under N_2H_2. A chemical evaporation of aluminium is then processed on both sides of the wafer: for the collected grid on the P^+ emitter and for the ohmic contact on the rear side (followed by an annealing).
The complete structure is shown in Fig.3

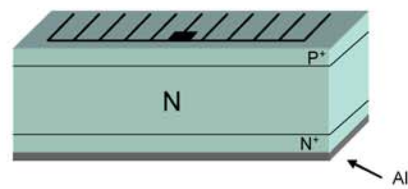

Fig.3 Schema of a solar cell

RESULTS AND DISCUSSION

After the BF_3 plasma implantation and the activation annealing, wafer sheet resistance is measured to define the doping activation and the conductivity type of the layer. A Cascade four points probe coupled with Keithley precision multi-meter were used.
Table 2 gives the corresponding results.

Acceleration voltage (kV)	1	5	10
Sheet Resistance (Ω/sq)	456	294	262

Table 2: Sheet resistance measurements

The Spreading Resistance Profile (SRP) obtained with an N-Type Cz (100) sample implanted by PULSION® at an acceleration voltage of 10 kV and a dose of $5x10^{15}$ at/cm² is shown in Fig.4.
At such energy, junction depth seems to be located at around 150 nm from the surface. Moreover, we observe that the maximum concentration measured is about 2E19 cm-3. This result is surprising as it is lower than expected. There is only partial diffusion of boron atoms probably due to the annealing, with a target temperature superior at the real temperature. Others analyses are in hand.
Secondary Ion Mass Spectrometry (SIMS) profiles of PULSION® BF_3 5 kV 1e15 at.cm^{-2} are presented in Fig.5. They compare the as-implanted boron profile, with the one obtained after a classical annealing at 950°C during 30 minutes. Few diffusion is observed compared with the theoretically calculated diffusion length:

$$Ldiff = \sqrt{Dt} = 0.02\ \mu m$$

As we can expect, the junction depth is lower (75 nm@1E18 cm^{-3}) at 5 kV than at 10 kV.

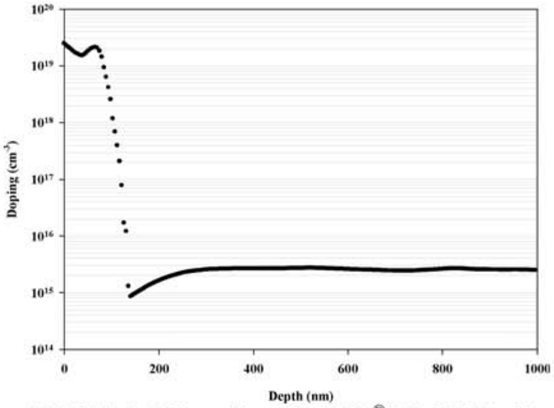

FIGURE.4: SRP profile: PULSION® BF_3 10kV and annealed sample

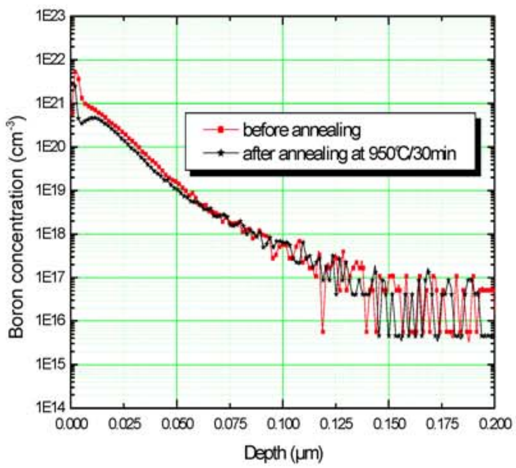

FIGURE 5: SIMS profiles PULSION® BF_3 5kV

Electrical characterisations like I-V measurements under sunlight and spectral sensitivity inform us about photovoltaic properties of our different photodiodes.

Fig. 6 compares the internal quantum efficiency of different photodiodes versus the incident wavelength.

Solar cells realised by PIII show better internal quantum efficiency than a conventional Fz solar cell in the short wavelength i.e. in the range 400-700 nm. This result is due to a shallower emitter obtained by PIII (150 nm at 10 kV) than in a conventional one which is around 300 nm. Table 3 presents some electrical properties under sunlight of PIII solar cells.

We can see that minority carrier diffusion length value is about 250 µm, which indicates a rather low metallic contamination.

Electrical Properties	1 kV	5 kV	10 kV
Voc(mV)	477	590	568
Jsc (mA/cm^2)	16.07	23.4	29
Length Diffusion(µm)	261	232	210
Sheet Resistance(Ω)	1.02	0.53	0.4
Shunt Resistance(Ω)	20.58	564	1454

Table 3: Electrical Properties under sunlight of PIII solar cells.

In the case of shunt resistance, 5 kV and 10 kV solar cells have acceptable values. Only 1 kV solar cell has a low shunt resistance but this is probably due to process contamination of the sample edge.

Voc and Jsc values reveal to be slightly lower than those expected. However we can easily optimise the process by passivating the surface and improving the front side metal grid, with an adjunction of a proper anti reflective layer. This should also result in a decrease of the sheet resistance and an increase of the shunt resistance, leading to a better behaviour of the solar cells.

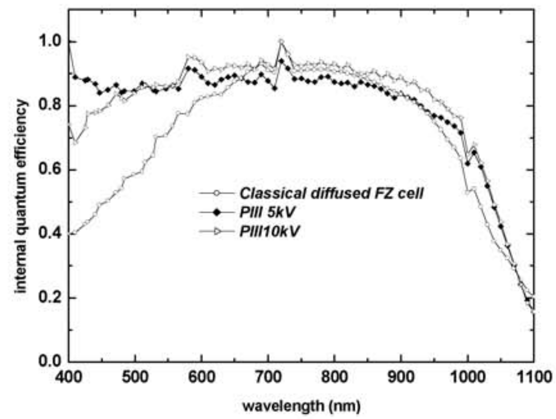

FIGURE 6: Internal quantum efficiency results obtained on PULSION® solar cells

Light Beam Induced Current (LBIC) scan map is presented in Fig.7a. Fig 7b gives a map of minority carrier diffusion lengths L_{diff}, extracted from LBIC results. We can see that even if the global value is around 250 µm, we obtain more than 300 µm (corresponding to the thickness of the samples) in many of grains.

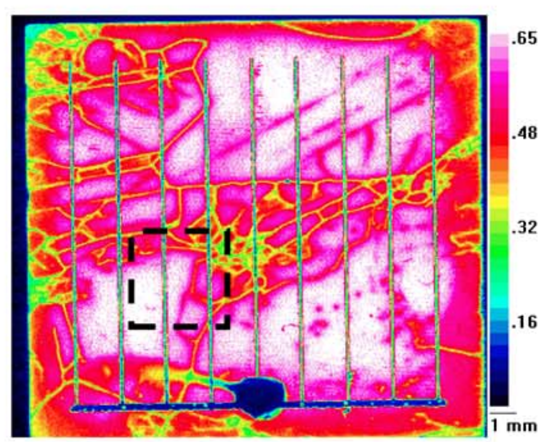

Fig. 7a PULSION® solar cell LBIC scan map (white light)

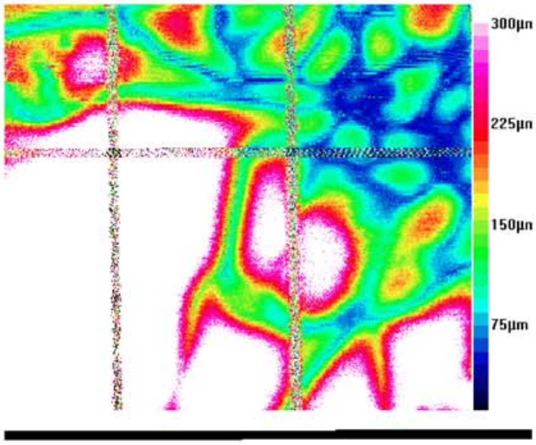

Fig 7b PULSION® solar cell map of L_{diff} (zoom)

SUMMARY

Solar cells have been realised by plasma immersion ion implantation at different acceleration voltage on N-type poly crystalline silicon. SIMS profiles and SRP measurements have shown that PIII prototype, PULSION®, was able to realise shallow junctions and more specifically thin emitters for a photovoltaic application. The electrical properties obtained show a satisfying photovoltaic behaviour.

The spectral variation of the internal quantum efficiency is practically constant in the short wavelength, due to the thickness of the emitter. LBIC scan maps have shown that grains present very good properties.

In conclusion, thanks to the lower cost of the equipment, and thanks the fact that implant time is independent from the surface, PIII technique seems to be a good candidate for the realisation of low cost solar cells.

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