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## A new approach to photovoltaic junction formation by using pulse implantation doping technique

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**Résumé.** — L'article présente la première démonstration d'une nouvelle méthode de formation de la jonction photovoltaïque p-n dans le silicium par la technique de « Dopage par Implantation Pulsée — Pulse Implantation Doping (PID) ». Dans cette technique une impulsion intense d'ions apporte aussi bien la dose nécessaire pour le dopage que l'énergie nécessaire pour la recristallisation de la couche de surface. Le faisceau pulsé (durée dans le domaine des microsecondes et de densité de courant de l'ordre de plusieurs kA/cm<sup>2</sup>) est engendré par le « Rod Plasma Injector », machine développée à INR pour les recherches de fusion contrôlée. Les meilleures cellules solaires obtenues dans un processus DIP non-optimalisé, avec le bore comme dopant ont, dans la condition AM1 des rendements de 4,5-4,7 % sans la couche antireflet.

**Abstract.** — The paper presents the first demonstration of a new method of forming photovoltaic p-n junction in silicon by the « Pulse Implantation Doping (PID) » technique. In this technique, an intense ion pulse provides both the dose necessary for doping and the portion of energy required to recrystallize a damage-free, doped surface layer. The ion beam pulses within the range of one microsecond and of a current density within the range of several kA/cm<sup>2</sup> are generated by a Rod Plasma Injector — the machine developed at INR — Świerk for the research in controlled ion beam fusion. The best solar cells obtained using a non-optimized PID process with boron as dopant have efficiencies of 4.5-4.7 % without antireflection coating at AM1 condition.

**1. Introduction.** — A significant effort in the development of ion implantation technique is now being directed towards the reduction of the costs of p-n junction formation, especially in connection with the prospect of mass production of photovoltaic cells. For example, Muller *et al.* [1] have adopted a simplified accelerator structure without mass separation, the ions being produced by DC glow discharge in a gas containing the dopant (BF<sub>3</sub> and PF<sub>5</sub>). By combining this simplified implantation process with the subsequent laser pulse annealing, they were able to fabricate silicon solar cells having conversion efficiency as high as 11 to 14 %.

In this paper, we present the results of the first demonstration of an entirely new approach to the p-n junction formation, referred to as Pulse Implantation Doping technique in which implantation and damage annealing are combined in a single processing step,

due to the use of a high intensity pulsed ion beam. In PID, the ion pulse provides the dose necessary to dope the semiconductor and, simultaneously, supplies an energy portion necessary to recrystallize the damage-free, near-surface layer [2]. In addition, likewise in the reference [1] the magnetic separation is also eliminated. This new approach is based on the use of powerful ion plasma guns, originally developed at INR-Świerk for the generation of ion beams used in thermonuclear fusion research [3, 4].

Below are presented considerations of the physical conditions of PID process, the experimental system, and the results of our pilot experiments on the p-n junction formation by boron implantation into n-type silicon.

**2. PID process conditions.** — At the moment, the PID process may be accomplished through the use of a

dopant in gaseous form (see Sec. 3.1). The considerations given below apply to boron doping, using  $\text{BF}_3$  gas. The mean ion energies, attainable in the experiments, amount to several keV and the pulse duration is in the range of one microsecond.

The nuclear component of the stopping power for boron in silicon in this energy range exceeds several times the electronic. Consequently, most of the beam energy is used for a direct heating of the crystal lattice, unlike the case of the laser or electron beam where the primary process consists in the formation of dense electron-hole plasma. Other types of radiation produced by the source (X-rays, light, electrons) deliver a negligible amount of energy as compared to the kinetic energy of the ion beam (see Sec. 3.1).

Therefore, we assume that the non-thermal effects [5] play a minor role in the PID process, which can be thus considered as a thermal phenomenon (solid-state epitaxial regrowth [6] or melting of the sample and its subsequent recrystallization). We adopt the latter approach since it is much better substantiated in the literature. Such an approach permits us to estimate the upper and the lower limits of the beam-energy density within which the PID process leads to the formation of the doped, recrystallized near-surface layer.

The lower limit  $E_{\min}$  is obtained by the condition of surface melting. Following Bell's considerations on the laser annealing of silicon [7], we conclude that for the available ion energies and pulse duration, the temperature evolution in the sample is dictated by heat diffusion. In such a case the maximum surface temperature is given by :

$$T_{\max} = \frac{2 I_0}{K_s} \left( \frac{k_s \cdot \tau_p}{\pi} \right)^{1/2} = \frac{2 E}{K_s} \left( \frac{k_s}{\pi \cdot \tau_p} \right)^{1/2}$$

where :

$I_0$  — beam power density, assumed to be constant during the pulse duration (i.e.  $E = I_0 \cdot \tau_p$ , where  $E$  — energy density of the pulse),

$K_s$  — mean value of the thermal conductivity of silicon over the temperature range of interest (0.64 W/cm.K),

$k_s = \frac{K_s}{\rho \cdot C_s}$  — diffusivity,

$\rho$  — specific density (2.33 g/cm<sup>3</sup>),

$C_s$  — specific heat (0.95 J/g.K),

$\tau_p$  — pulse duration.

Hence, the minimum energy density of the beam is :

$$E_{\min} = T_m \frac{(\pi C_s \cdot \rho \cdot K_s)^{1/2}}{2} \cdot \tau_p^{1/2},$$

where  $T_m$  — melting temperature.

The upper limit  $E_{\max}$  of the beam energy density is set by the requirement that the thickness of the silicon target, evaporated during the pulse —  $d_{\text{ev}}$ , must be small when compared to the desired thickness

of the recrystallized layer —  $d_{\text{rec}}$ . Taking  $d_{\text{rec}} = 0.2 \mu\text{m}$  and  $d_{\text{ev}} = 0.01 d_{\text{rec}}$ , and using the known formulae on the dependence of the evaporation rate on vapour pressure and the tabulated values of silicon vapour pressure [8], we obtain the values of  $E_{\max}$  for various pulse durations.

The energy density of the beam  $E$  is related to the boron dose  $D$  by the relation

$$D \simeq \frac{1}{4} \frac{E}{\varepsilon},$$

where  $\varepsilon$  — mean ion energy and  $1/4$  — a factor accounting for the plasma-jet composition (one B ion per three F ions). The values of  $E_{\min}$ ,  $E_{\max}$  and the corresponding values of  $\varepsilon$  are given in table I for various pulse durations and doping levels.

In view of simplifications introduced into above analysis, the estimations presented in table I should be considered as « entry » data for the experiment rather than as the results of rigorous theoretical treatment.

Table I. — *Parameters of the PID process for boron from  $\text{BF}_3$ , estimated on the basis of thermal melting model.*

Boron Dose [cm <sup>2</sup> ]	$\tau_p$ [ $\mu\text{s}$ ]	Pulse Energy Density [J/cm <sup>2</sup> ]		Ion Energy (keV)	
		$E_{\min}$	$E_{\max}$	$\varepsilon_{\min}$	$\varepsilon_{\max}$
$1 \cdot 10^{14}$	0.2	0.79	14	12	21
	0.5	1.3	21	20	33
	1.0	1.8	3.0	28	46
$5 \cdot 10^{14}$	0.5	1.3	21	3.9	6.6
	1.0	1.8	3.0	5.6	9.2
	2.0	2.5	4.0	7.8	12.0
$10^{15}$	1.0	1.8	3.0	2.8	4.6
	2.0	2.5	4.0	3.9	6.2
	5.0	4.0	5.3	6.2	9.5
$5 \cdot 10^{15}$	1.0	1.8	3.0	0.56	0.93
	2.0	2.5	4.0	0.78	1.23
	5.0	4.0	6.1	1.24	1.89

### 3. Experimental. — 3.1 PULSED ION BEAM SOURCE.

— The ion source, referred to as Rod Plasma Injector (RPI), is shown schematically in figure 1. The working gas ( $\text{BF}_3$ ) is injected into the vacuum chamber, evacuated to  $1 \times 10^{-5}$  torr, through a fast electromagnetic valve and expands in the electrodes region.

After an adjustable delay, a discharge is triggered between coaxial, cylindrical grid-type electrodes. The ions, produced in the discharge, are accelerated by the interelectrode radial electric field in the presence of a strong azimuthal magnetic field accompanying the discharge current flow. In the discharge conditions, the magnetic field influences, only slightly, the motion of heavy charged particles (ions) while the electron flow between the electrodes is strongly suppressed.

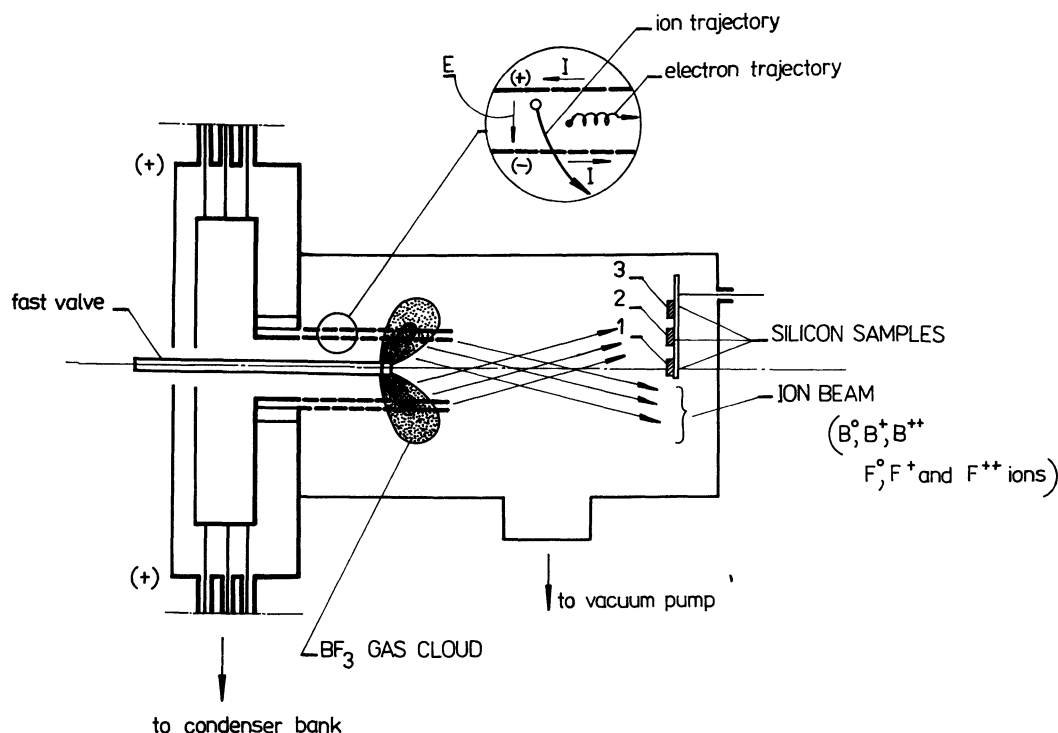


Fig. 1. — Schematic presentation of Rod Plasma Injector.

The idea of RPI device [3] is based on the well known fact that cycloidal trajectories of ions, moving in crossed electric and magnetic fields, are much larger than those of electrons. With the electron current flow lowered by self magnetic fields, acceleration of the ion component becomes very effective. At the moment, the energetic efficiency of ion acceleration reaches 10% for  $D^+$  ions.

The experimental conditions are monitored through current-voltage transients in the electrode circuit. Typical transients are shown in figure 2. The high energy ions are produced during the short interval when the discharge current falls as the ionized gas leaves the interelectrode region.

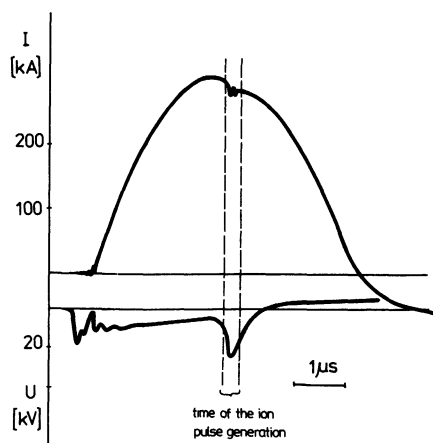


Fig. 2. — Typical current and voltage transients in the RPI device.

To give an idea of the size of the device, we present some basic dimensions and parameters :

- inner electrode diameter — 90 mm,
- outer electrode diameter — 130 mm,
- electrode length — 200 mm,
- condenser bank capacity — 21  $\mu$ F,
- condenser bank voltage — 35 kV.

The most important operational parameters of the ion source are the energy density at the target location, the mean ion energy and the ion energy spectrum.

The energy density of the incident ion pulses  $E$  has been measured by placing the calorimeter in the position of the implanted sample and has been found to vary between 3.0 and 3.5 J/cm<sup>2</sup>. The mean ion energy  $\epsilon$  has been estimated by comparing this value of pulse energy with the surface concentration (dose) of boron atoms, measured electrically. With  $E = 3.5$  J/cm<sup>2</sup> and  $D = 1 \times 10^{15}$  cm<sup>-2</sup>, the result is  $\epsilon = 5.5$  keV.

Till now, we have been unable to measure correctly the energy spectrum of boron ions. Instead, we present in figure 3 the energy spectrum of deuterium ions produced in the same device under comparable experimental conditions [9]. In this case  $\epsilon \approx 20$  keV.

The ion pulse, produced in the plasma discharge, is accompanied by other types of radiation emission. Below, we present a short discussion of this radiation, together with the estimates of the upper limits of the energy delivered in that way to the target.

The analysis of the electrical processes in the discharge circuit shows that, out of the 13 kJ stored in the

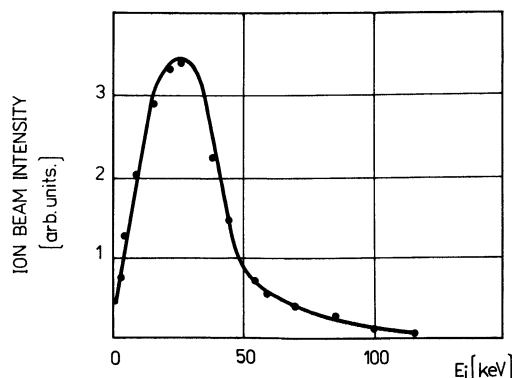


Fig. 3. — The energy spectrum of  $D^+$  ions produced in the RPI device.

condenser bank, only about one half of a kilojoule is released in the discharge and the rest is dissipated in the passive components of the circuit. No more than 50 % of this portion of energy has the form of electromagnetic radiation, including UV and X-ray radiation. This means that the upper limit of the electromagnetic energy density at the target location is  $0.06 \text{ J/cm}^2$ .

The ion component of the plasma-jet is accompanied by a neutralizing electron component. The spectroscopic and X-ray measurements on the RPI device [10] have revealed that the temperature of the electrons in the beam does not exceed 25 eV and hence, the energy delivered by electrons to the sample is less than  $0.02 \text{ J/cm}^2$ .

We conclude that the upper limit of the amount of energy reaching the sample in forms other than the kinetic energy of the ion beam does not exceed  $0.08 \text{ J/cm}^2$ , i.e. about 2.5 % of the total amount of energy delivered to the sample. Consequently, we feel justified in considering the effect of ion pulse on the silicon target in terms of a thermal model and disregard the effects of ionization.

### 3.2 SAMPLES AND EXPERIMENTAL PROCEDURE. —

The samples for the experiment were prepared of commercial n-type silicon wafers of resistivity 1 to 10 ohm cm and of  $\langle 111 \rangle$  orientation. For van der Pauw measurements the samples with photolithographically prepared « clover shape » patterns were used.

The samples were placed in a rotary holder, enabling them to be located at various distances away from the ion beam propagation axis. The distance between the samples position and the electrodes, measured along the beam axis, was 250 mm in all experiments.

The backscattering measurements of the implanted samples were performed using 1 MeV  $\text{He}^+$  ion beam. Solar cells were made of some of the samples implanted in the centre of the ion beam. The metallization of the cell electrical collectors, trimming and testing measurements were performed using standardized procedures used to evaluate experimental solar cells fabricated for the U.S. Dept. of Energy and Jet Propulsion Laboratory.

**4. Results and discussion. — 4.1 DOPED LAYER PROPERTIES. —** The monocrystallinity of the pulse implanted samples has been verified by Rutherford backscattering (RBS) measurements. All results of such analysis obtained thus far (7 samples) are similar to each other and a typical example is shown in figure 4. We observe, consistently, a very good monocrystallinity and a lack of damaged surface layer as indicated by almost perfect coincidence of the aligned spectra of the virgin and the implanted samples.

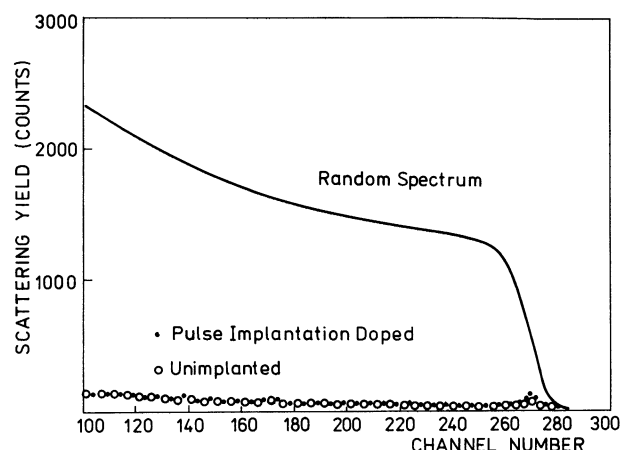


Fig. 4. — Typical Rutherford Backscattering spectra of silicon samples doped with boron by PID processes.

Under the conditions of our experiment, boron implantation is accompanied by fluorine ions and these ions, being heavier than boron ions, are potentially able to create damaged surface layer [1]. The lack of evidence of such a layer confirms our expectations of the melting mechanism being responsible for the good quality of the PID produced layer.

The results of electrical measurements are summarized in table II. This table shows the results obtained

Table II. — *Parameters characterizing the silicon layers implanted with boron using PID technique.*

$N_0$	$r$ [cm]	$\rho_B$ [ $\Omega/\square$ ]	$N_S$ [ $\text{cm}^{-2}$ ]	$u$ [ $\text{cm}^2/\text{Vs}$ ]	Type ness	$\chi_{\min}$ %
129	0	115	$8 \times 10^{14}$	67	p	4.2
130	2	351	$3 \times 10^{14}$	55	p	4.6
131	4	550	$2 \times 10^{14}$	56	p	3.8
132	0	219	$6 \times 10^{14}$	45	p	3.3
133	2	261	$3 \times 10^{14}$	67	p	3.7
134	4	348	$2.7 \times 10^{14}$	67	p	4.1

from six samples with three samples irradiated with each pulse. The parameters of the irradiating ion-beam pulses were not identical. The samples were placed at various distances  $r$  away from the beam axis as indicated in column 2 of table II. The next three columns give the values of sheet resistivity, carrier concentration and Hall mobility. The last column gives the values of  $\chi_{\min}$  — the normalized minimum scattering yield obtained in the course of RBS measurements, providing a measure of the crystalline imperfection of the investigated sample.

The first three rows exemplify a case in which it was possible to obtain the lowest values of sheet resistivity, although the range of the obtained values is wider than in the case of the second pulse (last three rows) which demonstrates the feasibility of obtaining an acceptable uniformity of implantation over a fairly large area.

Although it is obviously premature to specify, now, the values of the area possible to be implanted uniformly in the future, we would like to point out that they are dictated, to a large extent, by the very diameter of ion beam which in our case attains values of 10 cm and more.

The presented results show that it is possible to adjust the implantation conditions so that the sheet resistivity produced by PID process can reach values low enough to be useful in photovoltaic applications. By way of comparison, we would like to point out that, after room temperature implantation of  $10^{15} \text{ cm}^{-2}$  of 20 keV  $\text{B}^+$  ions from  $\text{BF}_3$  discharge without mass separation [1], the sheet resistivity of silicon was as high as  $10^4 \text{ ohm/sq}$  and to reduce it to a value in the range of  $10^2 \text{ ohm/sq}$ , it was necessary to anneal the sample at  $800^\circ\text{C}$  for 30 min.

The values of Hall mobility obtained in our experiments are typical for thermally or laser annealed samples implanted with identical doses of 35 keV  $\text{B}^+$  [11].

**4.2 SOLAR CELL PERFORMANCE.** — Table III summarizes the photovoltaic parameters of some of the fabricated cells having p-n junction formed by Pulse Implantation Doping of boron into n-type silicon using various number of the ion-beam pulses. The

Table III. — *Performance parameters of the solar cells fabricated by implanting boron into n-type silicon using PID technique.*

Sample No	Area $[\text{cm}^2]$	Number of pulses	A M O		A M I			
			Blue Resp. $[\text{mA/cm}^2]$	Red Resp. $[\text{mA/cm}^2]$	$V_{oc}$ [V]	$I_{sc}$ $[\text{mA/cm}^2]$	FF	$\eta$ %
157	1.49	1	7.9	13.9	0.484	18.5	0.5	4.5
164	1.60	1	6.8	13.3	0.406	17.4	0.35	2.5
165	1.50	3	—	—	0.468	19.4	0.42	3.8
169	1.57	5	8.9	15.0	0.486	20.1	0.48	4.7
172	1.70	3	6.9	12.3	0.218	17.2	0.27	1.0

open circuit voltage  $V_{oc}$ , short circuit current  $I_{sc}$ , fill factor  $FF$  and conversion efficiency  $\eta$  were measured under an illumination of AM1 radiation intensity. Figure 5 shows the current-voltage characteristics of the best cell obtained so far, illuminated under AM1 condition. The blue and red responses of a reference cell with conventionally diffused junction were at AMO-10-11  $\text{mA/cm}^2$  and 15-16  $\text{mA/cm}^2$ , respectively.

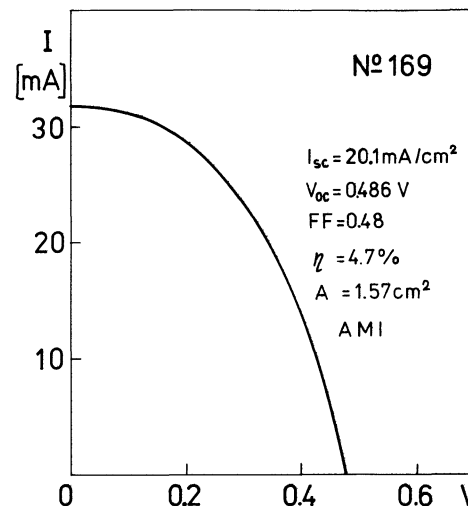


Fig. 5. — AM1 illuminated output characteristic of the cell with p-n silicon junction formed by Pulse Implantation Doping technique.

As we may see in table III, there is no correlation between the number of the applied ion pulses and the properties of the cells. This suggests that the cell performance parameters are determined by structural flows rather than by a doping concentration of the p-type top layer. Of all the parameters, only red responses and, to some extent, short circuit currents are acceptable for devices without AR coating. The low  $FF$  and  $V_{oc}$  are indicative of two problem areas in this case, a high series resistance and an excessive dark leakage current. The series resistance can be lowered by making an appropriate front contact pattern. Since the sheet resistance of the doped layer is usually larger than  $100 \text{ ohm/square}$  (see Table II), it is obvious that the number of fingers in the contact grid must be increased as compared to 8 lines employed in the present cells.

To lower the leakage current, the effort must be expanded in two directions. Firstly, the PID process has to be optimized as regards the ion-beam energy density and the beam homogeneity must be improved. Secondly, the metallization process parameters must be matched to the p-n junction depth and to the surface resistivity of the PID processed samples.

Further studies in these directions are in progress in our laboratory.

**5. Conclusions.** — The results obtained thus far demonstrate the feasibility of effective doping of the

semiconductor by pulse implantation in a genuine one-step process requiring no further thermal, laser or electron beam annealing. The solar cell efficiencies of 4.5-4.7 %, while substandard, are encouraging since they are obtained in non optimum conditions and there are a variety of means to increase their values to a satisfactory level. In view of its high energetic efficiency, high speed and ease of scaling-up the dimensions of the processed material (100 cm<sup>2</sup> in a single step seems to be feasible at the moment), the PID process seems to be well suited for mass-scale formation of photovoltaic p-n junctions.

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