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Phosphorus emitter engineering by plasma-immersion ion implantation for c-Si solar cells

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ABSTRACT

Ion Beam Services (IBS) has developed processes dedicated to silicon-based solar cell manufacturing using a plasma-immersion ion implantation equipment. It enables the realization of various doping profiles for phosphorus-doped emitters which fit the requirements of high-efficiency solar cells. PH_3 plasma-implanted emitters are chemically, physically and electrically characterized to demonstrate their excellent quality. Those emitters are then integrated into a low cost p-type monocrystalline silicon solar cell manufacturing line from the National Solar Energy Institute (INES) in order to be compared with usual $POCl_3$ diffusion. Starting from a basic process flow with blanket emitter and conventional full-area aluminum back-surface field, plasma-immersion implanted emitters enable to raise conversion efficiencies above 19.1%. Thanks to an optimized double layer anti-reflective coating, a 19.4% champion cell has been achieved. Depending on different plasma process parameters, lightly doped emitters are then engineered aiming to study doping modulation using a dedicated laser.

1. Introduction

Over the past few years, high conversion efficiencies above 19% have been achieved on p-type 156 mm c-Si substrates with beamline implanters dedicated to PV manufacturers [1,2]. Compared to diffusion-based doping processes, ion implantation offers a better control of the implanted dose and profile, while ensuring great uniformity and reproducibility [1]. However, the industrial integration of such a technology is rather slowed down by high implementation and running costs, since it still requires a thermal annealing step for defects healing and electrical activation of dopants [3]. Furthermore, throughputs as high as 3600 cells/h are required to fulfill the expectations of the roadmaps from the photovoltaic industry for solar cell manufacturing [4]. Plasma immersion ion implantation (PIII) reactors promise higher throughput, less investment costs and lower cost of ownership. Unlike beamline implantation, doping duration is not dependent on the implanted surface and it also offers the capability of a conformal doping, which is of particular interest for advanced textured surfaces [5] and cell architectures. IBS has developed, over the last 10 years, its own plasma doping tool. PULSION®'s key feature is a proprietary remote radio frequency plasma source that enables high density plasmas with a low chamber pressure. It results in a wide process space and a specific chamber design that optimizes the doping uniformity (cf. Fig. 1) [6].

Although the first publication from IBS about PIII for crystalline silicon solar cells dates back to 2004 [7], only few papers have since been published about emitter implantation through plasma immersion [8]. Whereas IBS and INES demonstrated the strong relevance of PIII for high efficiency silicon solar cells [9], this paper studies the ability and flexibility of this immersion plasma implanter to perform emitter doping for high efficiency crystalline silicon solar cells. The influence of the emitter doping profile is observed through modeling and characterizations. Optimized emitters are then implemented within a low cost solar cell manufacturing process flow which enables a comparison with usual $POCl_3$ diffused emitters. We then go ahead in the doping engineering by addressing the issue of emitter differential doping based on PIII.

2. Emitter modeling and simulation

In this part we are focused on modeling emitters and solar cells using PC1D, a software which enables modeling semiconductor

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devices and simulating their electrical behavior [10,11]. The aim of this study is to get a clear understanding of the influence of the emitter doping profile on the solar cell performances.

As an initial approach, the implanted homogeneous emitter has been modeled with complementary error functions even if we will see that the distribution of phosphorus diffused into silicon has a “kink-and-tail” shape [12]. In the complementary error function, depth and level of emitter doping are adjusted by the junction depth (X_J [nm]) and the surface concentration (C_S [at/cm^3]). Our calculation takes notably account of the impact of the dopant surface concentration on the front surface recombination velocity (*FSRV* [cm/s]) as observed by Cuevas through the linear approximation: $FSRV = 10^{-16}\ \text{cm}^4\text{s}^{-1} \times C_S$ (if $C_S \geq 10^{18}$ at/cm^3) [13]. In the same way, our calculation takes into account the degradation of the fill factor (*FF*) caused by increasing emitter sheet resistance. An empirical approximation is implemented within the model to make a link between the contact resistance (R_C in Ωcm^2) and the sheet resistance (R_{sq} in Ω/sq) of the emitter for dopant surface concentrations between 10^{20} and 10^{21} at/cm^3: $R_C = -0.0275 + 0.000445\ \text{cm}^2 \times R_{sq}$ (if $R_{sq} > 64\ \Omega$/sq), otherwise $R_C = 0.001\ \Omega\ \text{cm}^2$ [14].

Fig. 2 shows the variation of respectively the emitter sheet resistance and the conversion efficiency (*CE*) according to C_S and X_J. Through the comparison between the two diagrams, we see that the conversion efficiency is maximum for emitter sheet resistances around 60 Ω/sq. Moreover, improvement of the metallization paste will decrease the contact resistance. Thus that should enable engineering of less doped (around 100 Ω/sq) and shallower emitters which enhance the blue response of the devices. In this way, pairing of implantation and thermal annealing adds some process flexibility to design tailored fit emitters.

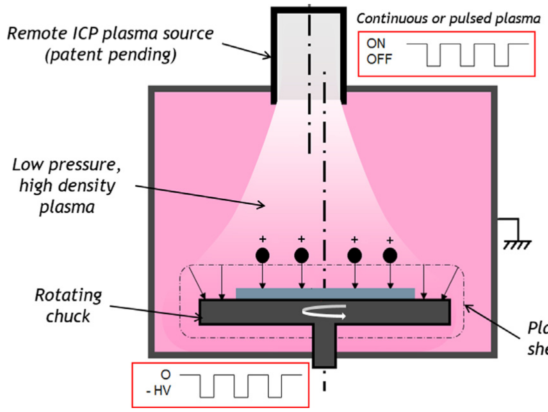

Fig. 1. Functional diagram of PULSION® ion implanter. Key features are a remote plasma source and a biased substrate being immersed in the plasma.

3. Description of experiments

This paper highlights the process development of plasma-immersion ion implantation for the fabrication of phosphorus homogeneous emitters. All the implantation experiments have been performed with a high productivity tool designed for the semiconductor industry. Phosphine (PH_3) has been chosen as the gas precursor required to create the phosphorus based plasma. Initially, Secondary Ion Mass Spectrometry (SIMS) analyses were performed on polished silicon wafers to understand the behavior of phosphorus and hydrogen in silicon before and after thermal annealing. Healing the defects generated by the implantation is a key target to fulfill during annealing. Thus, Transmission Electron Microscopy (TEM) has been carried out before and after oxidizing annealing to confirm the integrity of the silicon bulk crystal.

PULSION® implantation of emitters has then been embedded in an industrial low cost process flow of monocrystalline silicon solar cells fabrication (cf. Fig. 3). INES supplied IBS with textured and cleaned p-type silicon wafers for homogeneous phosphorus implantation. The wafers were then shipped back for annealing and completion of the fabrication process. Note that the post-implantation thermal annealing includes the growth of a passivation oxide that inherently enhances the open-circuit voltage compared to the classical $POCl_3$-based process (with single silicon nitride passivation on the front side). INES finally performed lifetime measurements and electrical characterizations of the fabricated solar cells so as to compare plasma immersion implantation to their standard $POCl_3$ diffusion process with and without subsequent oxidation step, as highlighted by the diagram of the Fig. 3 below.

It is noteworthy that no additional cleaning has been performed between implantation and annealing steps. Indeed, neither the transport between INES and IBS nor the non-mass analyzed implantation expose the material to contamination which would significantly impact the effective lifetime of photo-carriers. Contamination is regularly monitored in combination of Vapor Phase Decomposition (VPD) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Surface concentrations of metal contaminants are usually lower than $10^{10}\ \text{cm}^{-2}$ and almost never exceeds the $10^{12}\ \text{cm}^{-2}$ threshold on PH_3-implanted wafers.

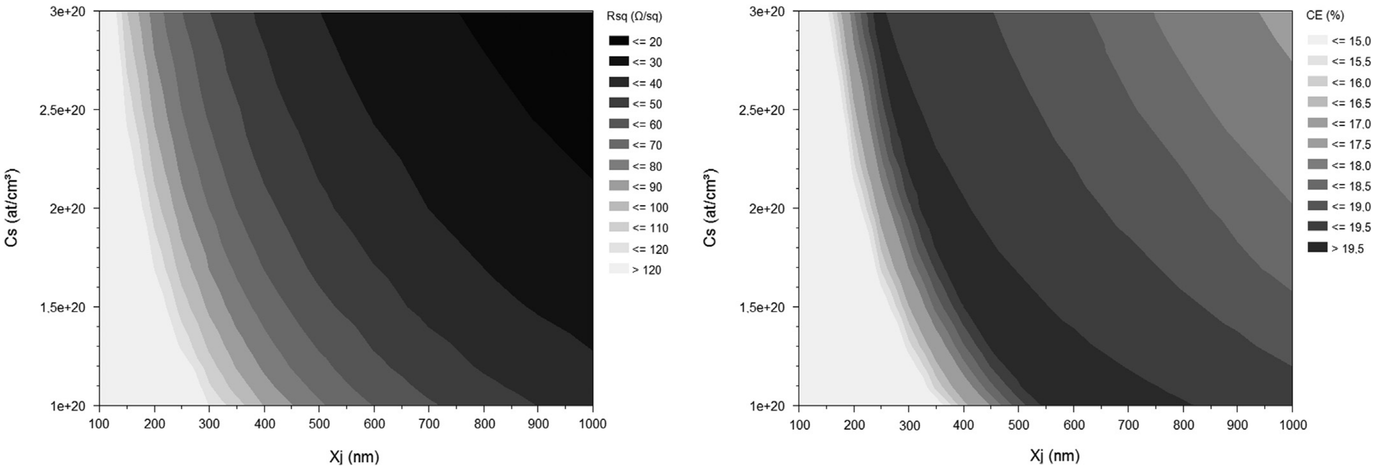

Fig. 2. Contour plot of PC1D-simulated emitter sheet resistance (R_{sq}) and conversion efficiency (*CE*), depending on junction depth (X_J) and surface concentration of dopants (C_S). Simulated efficiencies are optimal when emitter sheet resistances are around 60 Ω/sq.