IOP PUBLISHING JOURNAL OF PHYSICS D: APPLIED PHYSICS

J. Phys. D: Appl. Phys. **40** (2007) 2728–2731 doi:10.1088/0022-3727/40/9/008

Influence of the organic solvents on the properties of the phosphoric acid dopant emulsion deposited on multicrystalline silicon wafers

D Bouhafs[1], A Moussi[1], M Boumaour[1], S E K Abaïdia[1], L Mahiou[1] and A Messaoud[1]

[1] LCP/UDTS, 2 Bd. Frantz Fanon, BP 399, Alger-Gare, Algiers, Algeria
[2] Laboratoire des Matériaux, Minéraux and Composites, Université M'hamed Bougara, Avenue de l'Independence, 35000 - Boumerdès, Algeria

E-mail: bouhafsd@yahoo.fr

Received 13 December 2006, in final form 5 March 2007
Published 19 April 2007
Online at stacks.iop.org/JPhysD/40/2728

Abstract
This study is devoted to the formation of an n^+p emitter for multicrystalline silicon (mc-Si) solar cells for photovoltaic (PV) application. The atomization technique has been used to make the emitter from H_3PO_4 phosphoric acid as a doping source. The doping emulsion has been optimized using several organic solvents. H_3PO_4 was mixed with one of these solutions: ethanol, 2-butanol, isopropanol alcohol and deionized water. The volume concentration of H_3PO_4 does not exceed 20% of the total volume emulsion. The deposit characteristics of the emulsion change with the organic solvent. H_3PO_4 : 2-butanol gives the best deposited layer with acceptable adherence and uniformity on silicon surface. Fourier transform infrared characterizations show the presence of organic and mineral phosphorous bonds in the formed layer. The obtained emitters are characterized by a junction depth in the range 0.2–0.75 μm and a sheet resistance of about 10–90 $\Omega/\square$. Such a low cost dopant source combined with a continuous spray process can effectively reduce the cost per Wp of the PV generator.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The goal of the photovoltaic (PV) industry is the cost reduction of the PV generator to disseminate the solar energy utilization and consequently to respond to government programmes to achieve fixed targets in the renewable energy field. Concerning the PV generator which depends on silicon solar cells, both mono- and multicrystalline wafers, the main barriers to lowering the cost are firstly the silicon wafer price and secondly the cost of the fabrication process. Hence, it is necessary to reduce the step numbers and maximize their throughput for reducing the process cost of the silicon solar cell. It is well known that the most time and energy consuming is the cell emitter formation step when using phosphorus oxychloride ($POCl_3$) in a tube furnace. However, the cost and throughput of a $POCl_3$ diffusion system are not satisfactory because of the prolonged heat-treatment and excessive wafer handling, including wafer insertion into the quartz boat [1]. New technologies, for the emitter formation, were always the subject of research work with the aim of making solar energy competitive compared with other conventional sources. Spray and screen printing techniques show promising results from the point of view cost and mass production. Preu *et al* report in a study on the innovative production technologies for solar cells—SOLPRO that the total cost/Wp is 2.1€ with a reference process using $POCl_3$ phosphorous diffusion and 1.61€ with an innovative process using a screen printing technology [2]. In the last three years SPRAY technology has made a big impact

Table 1. Deposit parameters and characteristics of different doping emulsions on silicon surface.

	Wettability			
	Hot Plate 60 °C	Cold plate	Uniformity	Adherence
H_3PO_4 : IPA	Poor	Poor	Poor	Poor
H_3PO_4 : ethanol	Poor	Acceptable	Acceptable	Good on 70% of wafer area
H_3PO_4 : 2-butanol	Poor	Good	Good	Good on the whole wafer area

in the process of manufacture of the large surface solar cells in particular during the emitter formation step [3,4]. The electric characteristics of the emitters thus formed and the output of the cells obtained are comparable with those processed with the $POCl_3$ source [5–7].

2. Experiment

This is a first experiment that we undertook in this field with the aim of diversifying the doping sources in our laboratory. We chose the phosphoric acid H_3PO_4-like source of the phosphorus atoms to realize the n^+ layer. A diluted emulsion is prepared by mixing commercial phosphoric acid H_3PO_4 with water D.I. (H_2O) and other organic solvents. The concentration of the phosphoric acid varies between 5% and 20%. The H_3PO_4 acid is completely miscible with the solutions used and the emulsion is transparent.

Prior to deposit, saw damage on the as-cut multicrystalline silicon wafer was removed by etching in $NaOH/H_2O$ for 8 min followed by dipping in HF for 1 min and the obtained surface was hydrophobic. The deposit at an ambient temperature of the emulsion $H_3PO_4 : H_2O$ does not adhere to the surface of the plate. The atomized solution is presented in the form of large droplets on the plates. In spite of the passage at temperatures of deposit of 70 °C, we did not make a successful deposit. For this reason, the emulsion $H_3PO_4 : H_2O$ was eliminated. That necessitates the development of an adequate spray diffusion system [1]. We thus continued experiments with other organic solvents such as ethanol, 2-butanol and isopropanol (IPA) alcohol. Three doping solutions were prepared with a determined concentration of each component: organic solvent. The deposit was carried out by spin-on or spraying at the ambient temperature. We observed a good adherence and uniformity of the deposit on the whole of the wafer surface especially with H_3PO_4:2-butanol emulsion. Table 1 illustrates the deposit characteristics for each emulsion. For the H_3PO_4/IPA or H_2O we observe that the sprayed droplets do not wet the silicon surface but rather coalesce into balls of a few millimetres in diameter.

After the deposit, samples undergo a drying at 250 °C for 10 min in a conveyor furnace. The diffusion of phosphorus atoms was carried out in an open tube furnace at 850 °C for 20 min under nitrogen flux. Before resistivity measurements, the residual phosphoro-silicate glass (PSG) layer was removed in HF10%. One major difficulty with the dopant spray-on technique is the removal of the dopant residual layer on the wafer surface after the diffusion. One has to oxide the surface at 800 °C and a further HF dip is needed to obtain a clean and hydrophobic surface [6]. Also we can use the HF-Piranha etch-HF sequence [8] to clean the surface after a higher temperature firing step.

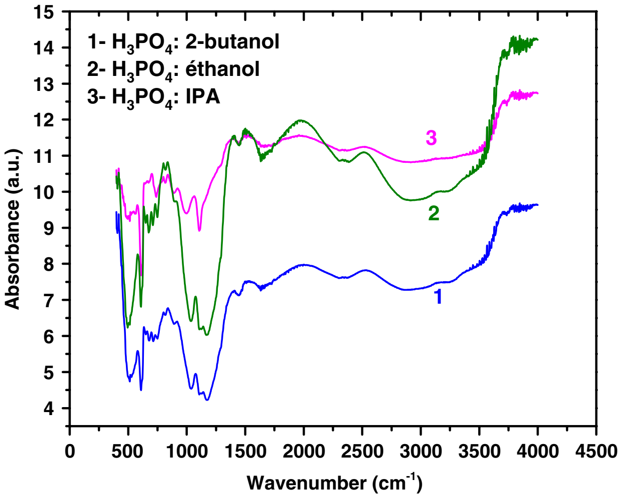

Figure 1. FTIR spectra of sprayed dopant layer on silicon after drying at 250 °C for 15 min using several emulsions.

3. Result and discussion

Fourier transform infrared (FTIR) characterizations were carried out using a Nexus Thermo Nicolet infrared spectrometer to identify the phosphorus molecules in the dried layers. The FTIR curves in figure 1 show presence of organic and mineral phosphorous bonds in the formed layer. Phosphorous organic bonds P–OR and P–O–C bonds are detected at 870/1110 cm^{-1} and 1190/1240 cm^{-1}, respectively. Mineral bonds such as P–OH: elongation, P–H and P=O are detected at 1600 cm^{-1}, 2280/2410 cm^{-1} and 1255/1285 cm^{-1}, respectively. After the high temperature firing the FTIR curves show the emergence of new absorption peaks in the spectral range 400–600 cm^{-1} as illustrated in figure 2. Investigations of the vibrational modes at 449, 465 and 528 cm^{-1} absorption peaks indicate that their origin can be attributed to thermal donors (TD1-TD6 species) due to oxygen related defects in bulk silicon [9]. It is well known that high-temperature processes applied to solar-grade multicrystalline wafers lead to a drastic degradation of minority carrier life time via the electrical activation of oxygen related defects [10–12]. On the other hand, some authors [13–15] attribute this behaviour to the dissolution of the precipitates, which contain metal transition elements such as copper and iron known as charge carrier lifetime killers.

Emitter characterizations of the elaborated n^+p emitters were performed by measuring sheet resistance with a fully automatic four point probe resistivity measurement system and the junction depth using an Accent Hall Profiling System HL-5900. Table 2 show the sheet resistivity values obtained with the different dopant emulsions. Figure 3 shows the corresponding emitter profiles at 850 °C for 20 min.

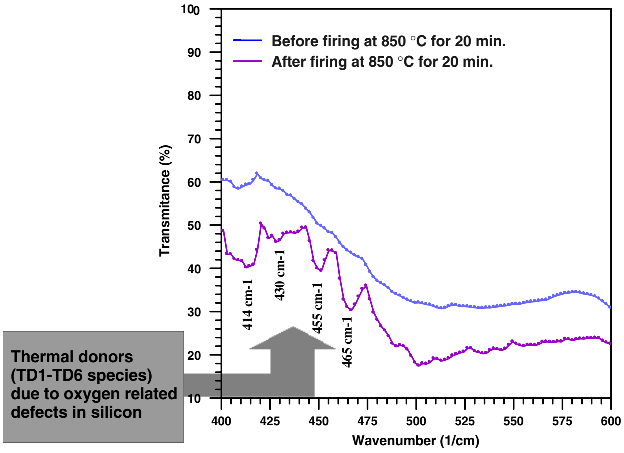

Figure 2. FTIR spectra of deposited layer before and after drive-in step.

Table 2. Sheet resistivity data versus organic solvents and annealing diffusion profile.

Sample number	Emulsion	R□ (Ω/□)	Standard deviation (Ω/□)
HP2-A	H_3PO_4 : IPA	62.3	5
HP2-B	H_3PO_4 : ethanol	70.7	6
HP2-C	H_3PO_4 : 2-butanol	86	4.5
HP9	—	35	3.0
HP11	—	10	4.3

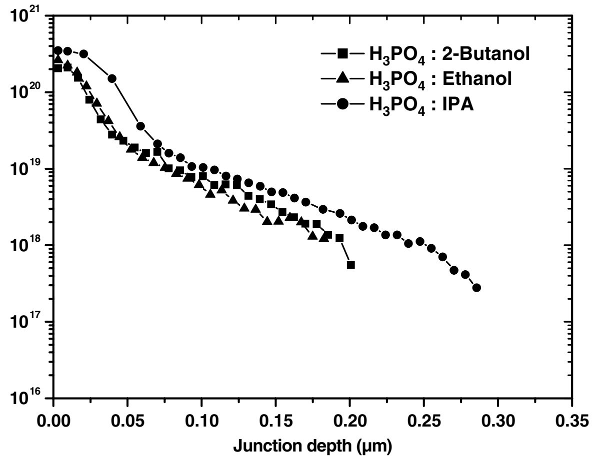

Figure 3. Hall profiles of phosphorus after diffusion in a tube furnace at 850 °C. The PSG layer was removed before measurement.

We observe that the emitter obtained with the H_3PO_4 : IPA solution is characterized by a depth of 0.32 μm and a surface concentration (N_s) of 3.5×10^{20} cm^{-3}. Emitters with emulsions, phosphoric acid/ethanol or 2-butanol present a depth of about 0.22 μm and a dopant surface concentration of 2.06×10^{20} cm^{-3} and 2.6×10^{20} cm^{-3}, respectively. These values of N_s are compatible with the screen printing technology in the photovoltaic industry. By adjusting the temperature and time in the diffusion process we can easily control the emitter parameters. HP9 and HP11 (table 2) annealed at 875 °C and 900 °C for 20 min have a junction depth of 0.5 μm and 0.75 μm, respectively. Using the elaborated n$^+$p emitters, 10×10 cm^2 mc-Si solar cells are manufactured, with the screen printing technology when front and back surface metallization contacts have been realized with silver and aluminium pastes, respectively. The electrical performances of the characterized cells under illumination (100 mW cm^{-2}, 25 °C) are illustrated in table 3. Cells have been realized without antireflection coating or passivating layers. From the short circuit current (J_{sc}) and open-circuit voltage (V_{oc}) values one can show the effect of the bulk lifetime of the mc-Si material which is in the range 7–10 μs and also the heavy doping effect in the n$^+$p region when comparing the measured values of 576.2 and 563.5 mV.

Table 3. Electrical performances of 10×10 cm^2 mc-Si solar cells under standard illumination.

Cell number	R□ (Ω/□)	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF (%)	η (%)
HP9	35	21.51	576.2	69.08	8.56
HP11	11	17.35	563.5	76.19	7.45

4. Conclusion

New low cost dopant emulsions for n$^+$p emitter formation on multicrystalline silicon wafer have been investigated. Phosphoric acid mixed with several organic solvents such as ethanol, 2-butanol and isopropanol alcohol has proved to be a cost-effective phosphorus doping source for the PV industry. Good adherence and uniformity of the deposit on the whole of the multicrystalline wafer surface are obtained with H_3PO_4 : 2-butanol emulsion.

FTIR characterization shows the presence of organic and mineral phosphorous bonds in the formed layer before and after the diffusion step. By adjusting the temperature and time in the diffusion process we can easily control the emitter parameters. n$^+$p emitters with a sheet resistivity range 10–90 Ω/□ and a junction depth from 0.2 μm to 0.75 μm were measured, respectively, on the samples. The electrical performances of the tested cells without surface texturing and antireflection/passivates layer present efficiencies of around 8% on a low material quality. Such a low cost dopant source combined with a continuous spray process can reduce effectively the cost per Wp of the PV generator.

Acknowledgment

This work was financed by the U.D.T.S /MESRS of Algeria.

References

[1] Kim D S, Hilali M M, Rohatgi A, Nakano K, Hariharan A and Matthei K 2006 *J. Electrochem. Soc.* **153** A1391–6

[2] Preu R, Lüdeman R, Emanuel G, Wetting W, Everstein W, Güthenke G, Untiedt D and Schweitzer G 2000 *16th European Photovoltaic Solar Energy Conf. (Glasgow, UK, 1–5 May 2000)*

[3] Herzog B, Rüland E and Fath P 2005 *15th Int. Photovoltaic Science and Engineering Conf. (Shanghai, China, 10–15 October 2005)*

[4] Moussi A, Bouhafs D and Mahiou L 2002 *7th World Renewable Energy Congr. (Cologne, Germany, 25 June–5 July 2002)*

[5] Bouhafs D, Moussi A, Boumaour M, Abaïdia S E K and Mahiou L 2006 *Thin Solid Films* **510** 325–8

[6] Herzog B and Peter K 2006 *22nd European Photovoltaic Solar Energy Conf. (Dresden, Germany, 4–8 September 2006)*

[7] Voyer C, Biro D, Emanuel G, Preu R, Kariath J and Wanka H 2004 *19th European Photovoltaic Solar Energy Conf. (Paris, France, 7–11 June 2004)*

[8] Kränzl A, Kopecek R, Peter K, Rüland E and Fath P 2004 *19th European Photovoltaic Solar Energy Conf. (Paris, France, 7–11 June 2004)*

[9] Emtsev V V Jr., Ammerlaan C A J, Emtsev V V, Oganesyan G A, Misiuk A, Surma B, Bukowski A, Londos C A and Potsidi M S 2003 *J. Cryst. Res. Technol.* **38** 394

[10] Möller H J, Long L, Werner M and Yang D 1999 *Phys. Status Solidi.* A **171** 175

[11] Gee J M *et al* 1997 *14th European Photovoltaic Solar Energy Conf. (Barcelona, Spain, 30 June–4 July 1997)*

[12] Möller H J, Ghosh M, Rinio M, Riedel S and Yang D 1995 *13th European Photovoltaic Solar Energy Conf. (Nice, France, 23–27 October 1995)* pp 1390–3

[13] Cabanel C and Laval J Y 1990 *J. Appl. Phys.* **67** 1425

[14] Fell T S, Wilshaw P R and Coteau M D d 1993 *Phys. Status Solidi* A **138** 695

[15] Higgs V and Kittler M 1993 *Appl. Phys. Lett.* **63** 2085