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

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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 $\text{H}_3\text{PO}_4$ phosphoric acid as a doping source. The doping emulsion has been optimized using several organic solvents. $\text{H}_3\text{PO}_4$ was mixed with one of these solutions: ethanol, 2-butanol, isopropanol alcohol and deionized water. The volume concentration of $\text{H}_3\text{PO}_4$ does not exceed 20\% of the total volume emulsion. The deposit characteristics of the emulsion change with the organic solvent. $\text{H}_3\text{PO}_4$ : 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 $\mu$m 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 ($\text{POCl}_3$) in a tube furnace. However, the cost and throughput of a $\text{POCl}_3$ 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 \textit{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 $\text{POCl}_3$ 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...
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 POCl3 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 H3PO4-like source of the phosphorus atoms to realize the n⁺ layer. A diluted emulsion is prepared by mixing commercial phosphoric acid H3PO4 with water D.I. (H2O) and other organic solvents. The concentration of the phosphoric acid varies between 5% and 20%. The H3PO4 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/H2O 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 H3PO4 : H2O 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 70°C, we did not make a successful deposit. For this reason, the emulsion H3PO4 : H2O 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 H3PO4 : 2-butanol emulsion. Table 1 illustrates the deposit characteristics for each emulsion. For the H3PO4 : IPA or H2O 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.
emitter parameters. By adjusting the temperature and time in the diffusion process we can easily control the surface concentration. 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 \(\mu s\) and also the heavy doping effect in the n+p region when comparing the measured values of 576.2 and 563.5 mV.

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\(_3\)PO\(_4\) : 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 \(\Omega cm\) and a junction depth from 0.2 to 0.75 \(\mu m\) were measured, respectively, on the samples. The electrical performances of the tested cells without surface texturing and antireflection/passivating layers 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

Influence of organic solvents on properties of acid dopant emulsion


