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Mass production of high efficiency selective emitter crystalline silicon solar cells employing phosphorus ink technology



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ABSTRACT

Phosphorus ink technology has been demonstrated as a simple and cheap method to realize selective emitter (SE) crystalline silicon solar cells through mass production in a professional photovoltaic company. We have achieved an average conversion efficiency (η) of 19.01% with peak η of 19.27% for the SE solar cells based on commercial-grade p-type silicon substrate, much higher than that of the homogeneous emitter counterparts whose average η is 18.56%. The standard deviation of the performance for these SE solar cells is also smaller, indicating better repeatability of the phosphorus ink SE technology. Moreover, the SE silicon solar cells can well adapt to various Ag pastes while preserving high cell performance, which offers an opportunity to choose a cheap Ag paste as front metallization material. With the aid of PC1D, we have shown that the η of the SE solar cells can be further improved as the sheet resistance in the illuminated area increases from the present value of 70 to 120 Ω/\Box .

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1. Introduction

For homogeneous emitter crystalline silicon solar cells, heavy doping to obtain good ohmic contact and low doping to avoid the formation of dead layer are insoluble contradictions to obtain high conversion efficiency. Fortunately, selective emitter (SE) structure which contains heavy doping area under front contacts and low doping area between fingers simultaneously provides good ohmic contact and high blue response [1]. Therefore, the SE silicon solar cell exhibits higher open circuit voltage (V_{OC}), better short circuit current density (I_{SC}), and enhanced conversion efficiency (η). Various methods have been proposed to prepare SE crystalline silicon solar cells, such as etch-back emitter [2-4], doped silicon ink [5-7], laser doped SE [8-13], ion implantation process [14], oxide, a-Si and porous silicon mask process [15-18]. Hallam et al. [19], have successfully achieved the η of the solar cells based on large area p-type Czochralski (Cz) silicon substrates as high as 19.4% utilizing the improved laser doped SE technology. Through rigorous process optimization, Sunrise Global Solar Energy [20] has announced that a highest independently confirmed η of 19.17% is obtained for the SE solar cells adopting the etch-back technology from Schmid. Antoniadis et al. [21], have demonstrated an average η of 18.9% with peak η up to 19% in 100 SE silicon solar cells employing silicon ink technology. Recently, screen printable phosphorus paste [22] has also been introduced to prepare SE silicon solar cells and an average η of 17.9% has been reached.

In general, there are several factors to be considered when applying SE technology to silicon solar cell in mass production scale. Firstly, the additional process steps should be minimal and the fabrication process does not dramatically deviate from the conventional fabrication process to make the approach costeffective and easy to implement [1]. Secondly, the standard deviation of the cell performances should be as small as possible since good repeatability is also important to maintain low fabrication cost. Thirdly, considering that silicon wafer and Ag paste are the main parts of the cost for crystalline silicon solar cells, the SE method should be efficient to increase the conversion efficiency of the solar cells using low grade wafers as substrates and cheap Ag pastes as front electrode material. Finally, the sheet resistance in the illuminated area should be optimized to obtain good blue spectral response without much degradation of fill factor.

Facing these challenges, in this study, we have demonstrated a simple method to realize SE silicon solar cells by a cheap homemade phosphorus ink technology, without mask, multiple diffusions, etch-back techniques, and laser ablation. We have achieved an average η of 19.01% (peak η of 19.27%) for the SE solar cells on commercial-grade p-type Cz silicon wafers in mass production with a good yield of 99.58%, small standard deviation of η (0.11%), and low fragmentation rate of 0.09% in the screen printing of phosphorus ink. Moreover, the SE solar cells can well adapt to

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various Ag pastes, providing an opportunity to choose a cheap Ag paste as front metallization material while maintaining high cell performance. With the aid of PC1D simulation, we have also proposed increasing the sheet resistance to $120 \Omega/\Box$ in the illuminated area to further improve the performance of the solar cells with the phosphorus ink SE technology.

2. Experimental details

2.1. Synthesis of phosphorus ink

The process for preparing phosphorus ink mainly includes three steps, i.e., purification, synthesis, and stir, using polyethylene glycol, ammonium phosphate, ethyl silicate, and nano-silicon dioxide as raw materials. Firstly, polyethylene glycol and ammonium phosphate were respectively diluted in deionized water, following the removal of metal impurity using 3M ZP400 ion exchange membrane, and then the distillation. Ethyl silicate and dispersing agent (mainly contains ethanediol and ethanol) also received purification by ion exchange membrane. Secondly, nanosilicon dioxide was mixed with polyethylene glycol in a Unix UM-125 stirring equipment with self rotation speed of 200 rpm and centrifugal rotation speed of 1200 rpm at room temperature, obtaining a mixture A. Ammonium phosphate was combined with ethyl silicate and ethanediol under ultrasonic wave at the temperature of 40 °C, achieving a synthesis of B. Finally, products A, B and nano-silicon dioxide were put together in the UM-125 stirring equipment to receive self/centrifugal rotation stir, forming the phosphorus ink.

2.2. Preparation of SE solar cells

Fig. 1 is a schematic diagram of the fabrication process for the reference and phosphorus ink SE solar cells. Both cells were prepared in mass-production-scale on a standard production line. All wafers used in this work were commercial-grade p-type pseudo-square (156 mm × 156 mm) Cz-Si wafers with an average thickness of 200 μ m and resistivity of about 2 Ω cm. The reference solar cells were manufactured by the standard fabrication method

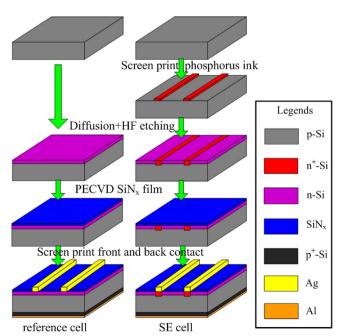


Fig. 1. Process sequence for the fabrication of the reference and phosphorus ink SE solar cells.

of the homogeneous emitter crystalline silicon solar cells. Firstly, the wafers were cleaned and textured in KOH solution to produce random pyramid surfaces. Then the wafers were put into a conventional diffusion tube furnace to receive n-type diffusion using POCl₃ as dopant source, achieving an average sheet resistance of 62 Ω/\Box . Subsequently, the wafers underwent edge junction isolation by ion etching, followed by the removal of phosphosilicate glass (PSG) through HF etching. After that, SiN_x coatings were deposited onto the wafer surfaces by plasma enhanced chemical vapor deposition (PECVD) system to act as antireflection and passivation layers. Finally, the front and back metallization of the wafers were carried out by screen printing technique and followed by baking and co-firing in a conveyer belt furnace.

The fabrication of the SE solar cells is similar to that of the reference solar cells except that the screen printing of phosphorus ink is added prior to the diffusion in tube furnace, which can be obviously seen in Fig. 1. Phosphorus ink was screen printed on the area where front metallization will be performed and then dried under 300 °C for about 1 min in a conveyer belt furnace. Subsequently, the wafers were put into a tube furnace subjected to the diffusion temperature of 900 °C only in N₂ atmosphere for heating duration of 16 min to form heavy doping at first, and then 845 °C in N₂ atmosphere which carries POCl₃ for heating duration of 10 min to form light doping. The average sheet resistance of the front contact area and illuminated area were 30 and 70 Ω/\Box , respectively. The residual phosphorus ink was removed in HF solution when removing the PSG. The following fabrication processes were exactly identical to those of the reference cells. It is clear that only one process step is added in the present phosphorus ink SE technology, and the whole fabrication process does not dramatically deviate from that of the reference solar cells.

2.3. Analysis methods

The viscosity of the phosphorus ink was measured by a LVDV-S viscometer at the temperature of 25 °C. The energy dispersive x-ray spectroscopy (EDX) was performed to examine the elements contained in the phosphorus ink after drying process. The Leica DM 2500M optical microscope was used to observe the phosphorus ink pattern. Current–voltage (I–V) tester was used to characterize the electrical performances of the solar cells under AM1.5 spectrum at the temperature of 25 °C. The surface reflectance and eternal quantum efficiency (EQE) of the solar cells were measured in 300–1100 nm wavelength range by PVE 300 photovoltaic device characterization system. We also employed PC1D simulation software to numerically calculate the EQE and I–V performance of the solar cells.

3. Results and discussion

3.1. Characteristics of the phosphorus ink

Fig. 2(a) shows a photograph of the phosphorus ink. It is a colorless liquid with density of 1.31 g/mL. Some important characteristics of our phosphorus ink are nontoxic, noncorrosive and nonflammable, which make it safe to be applied to production lines. The viscosity of the phosphorus ink is also very important since the gridline width of the screen printed phosphorus ink will increase when its viscosity is small, resulting in the enlargement of heavily doped region. Though the as-synthesized phosphorus ink is in liquid state, its viscosity can reach as high as 20,000 cps, which is sufficient for keeping the shape of the screen printed phosphorus ink. Generally, the deviation between the screen line width and printed ink width is smaller than 15 μ m. For instance, the printed phosphorus ink width is 190 μ m as the screen line

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