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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 $62 \Omega/\Box$. 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



Fig. 2. (a) A photograph of the phosphorus ink and (b) its EDX results.



Fig. 3. Photographs for the silicon wafer after (a) screen printed phosphorus ink, (b) PECVD SiN_x, and (c) screen printed front metal gridlines. The optical microscope pictures of the individual phosphorus ink (d) before PECVD SiN_x and (e) after screen printed front metal gridlines.

width is 180 μ m (see Fig. 3). Fig. 2(b) presents the elements contained in the dried phosphorus ink detected by EDX. The result indicates that only C, O, Si and P are residual after drying process at the temperature of 300 °C. Thereinto, P, as a dopant source, diffuses into silicon wafer at the temperature of 900 °C, whereas, C, O and Si are removed as the residues by HF etching.

3.2. Characteristics in fabrication process

Fig. 3(a)–(c) exhibits photographs for the silicon wafers after the screen printed phosphorus ink, PECVD SiN_x layer, and screen printed front metal gridlines, respectively. The screen printed phosphorus ink pattern can be evidently observed both before and after diffusion. Here, it is worth mentioning that we can easily alter the gridline width of the phosphorus ink by changing the printing plate to adapt to various screen printers in metallization process. Importantly, the cost of the phosphorus ink in each wafer is quite low, typically around 0.5–0.8 cent (about 0.0011–0.0018 \$/W). After the deposition of SiN_x coating, the phosphorus ink pattern becomes vague but still visible to the naked eyes. After the overprint of the front electrode, the phosphorus ink pattern where is not covered by the Ag gridlines is invisible to the naked eyes, but it still can be observed through optical microscope, as shown in Fig. 3(e), which is beneficial to check whether misalignment exists.

3.3. Comparison of the electrical parameters between the SE and reference cells

We have successfully applied the phosphorus ink technology to large batches of SE silicon solar cells fabricated on standard production lines. Fig. 4 exhibits the values of the V_{OC} , J_{SC} , FF and η for 1203 SE solar cells against 408 reference solar cells (Note that, the SE and reference solar cells were prepared in a typical experiment with the same condition for better comparison). Obviously, both the V_{OC} and J_{SC} of the SE solar cells are significantly higher than those of the counterparts, and their *FFs* are comparable. As a result, an average η of 19.01% for the SE cells has been achieved, 2.4% higher than that of the reference cells with an average η of 18.56%. Furthermore, the η of



Fig. 4. Electrical parameters (V_{OC} , J_{SC} , FF, and η) for 1203 phosphorus ink SE solar cells against 408 reference solar cells.



Fig. 5. I-V characteristics for the optimal phosphorus ink SE solar cell.

Table 1

PC1D calculated and experimental electrical parameters for the reference and phosphorus ink SE solar cells with a sheet resistance of 70, 120, and 170 Ω/\Box in the illuminated area. S. R., N_{Sr} , SRV, Cal., and Exp. represent the sheet resistance, phosphorus surface concentration, surface recombination velocity, calculated and experimental results, respectively.

Cell type	S. R. (Ω/□) (cm^{-3})	SRV (cm/s)	V _{OC} (mV)	J _{SC} (mA/ cm ²)	FF (%)	η (%)
Reference cells SE cells	Cal. 62 Exp. 62 Cal. 70 Exp. 70 Cal. 120 Cal. 170	$\begin{array}{c} 1.1 \times 10^{20} \\ - \\ 8.0 \times 10^{19} \\ - \\ 4.0 \times 10^{19} \\ 2.5 \times 10^{19} \end{array}$	40,000 - 9000 - 4000 2500	0.633 0.633 0.640 0.640 0.645 0.645	36.93 36.98 37.35 37.34 37.63 37.70	79.40 79.31 79.55 79.54 78.80 77.97	18.56 18.56 19.02 19.01 19.13 18.99

our optimal SE solar cell has reached as high as 19.27% with the V_{OC} of 0.641 V, J_{SC} of 37.67 mA/cm², and *FF* of 79.86%, as illustrated in Fig. 5.

As it is known, the enhanced J_{SC} is attributed to the improved blue spectral response in SE solar cells. The prominent increased V_{OC} can be explained from two aspects: on one hand, the sheet resistance of 70 Ω/\Box in the illuminated area for the SE cells is larger than that of the reference cells with a value of 62 Ω/\Box , leading to a decreased Auger recombination. On the other hand, the existence of heavily doped area under the front contact can greatly repel the minority carriers away due to the field-effect passivation [23]. Note that the metal–semiconductor contact is a high recombination area, thereby the surface recombination rate is reduced (the surface recombination rate reduced from 40,000 cm/s for the reference solar cells to 9000 cm/s for the SE solar cells, based on PC1D simulation, shown in Table 1). For the *FF*, the value of the SE solar cells is slightly higher than that of

the reference solar cells despite the larger sheet resistance in the illuminated area. This stems from the heavy doping under the front contact which results in a decreased contact resistance.

Furthermore, the standard deviation of the *FF* for the SE solar cells is 0.32%, whereas the value for the reference solar cells reaches 1.00%, leading to the smaller standard deviation of η (0.11%) for the SE solar cells. Therefore, the performance of the mass-produced SE solar cells with our phosphorus ink technology exhibits narrower distribution than that of the reference solar cells. We should note that this is significant since producing high efficiency solar cell in a steady level can help to reduce the cell cost. Furthermore, through mass production, we have achieved that 99.58% of the SE silicon solar cells possess efficiency higher than the average η (18.56%) of the reference cells, and the fragmentation rate is only 0.09% in the process of fabricating SE structure with a screen printing speed of 1100 wafers/h.

3.4. Metallization with different silver pastes

The dependence of the SE solar cell performance on silver paste has also been investigated in this study, as shown in Fig. 6. Silver pastes of DuPont PV17A, Heraeus SOL9600 and Shanghai Transcom TC298S were tested in mass-production-scale. Very narrow distribution of FFs has been observed in the SE solar cells with front metalized by these three types of silver pastes with average values exceeding 79.5%. It indicates that the contact resistance and junction recombination of all the cells are small, which is independent of the type of the silver pastes. This benefits from the heavy doping under the front contacts to make good ohmic contacts and p-n junctions deep enough to avoid metal puncturing through the junctions. Other electrical parameters (V_{OC} , J_{SC} , and η) of the SE solar cells also exhibit no much dependence on the silver paste. Therefore, the SE solar cells employing our phosphorus ink technology can be adapted to various silver pastes, which provides a chance to select a cheap silver paste while maintaining high solar cell performance. In addition, it should be noted that the silicon solar cells (both SE and reference) in this study are made in commercial-grade Cz silicon wafers for a low cost purpose. Since the silicon wafer and Ag paste are the two main parts of the cost in producing crystalline silicon solar cells, low-cost and high efficiency SE silicon solar cells can be realized by employing the present phosphorus ink technology. In fact, we have successfully employed the phosphorus ink SE technology in full capacity of 5 production lines in a local photovoltaic company since June, 2012.



Fig. 6. Comparisons of the electrical parameters for the phosphorus ink SE solar cells respectively screen printed PV17A, SOL9600, and TC298S silver pastes to form front metallization.



Fig. 7. PC1D calculated and measured EQE of the phosphorus ink SE solar cells with a sheet resistance of 70, 120, and 170 Ω/\Box in the illuminated area, together with the experimental reflectance.

3.5. Optimization of the sheet resistance in the illuminated area

In order to further improve the cell performance, we have employed PC1D software developed by the University of New South Wales to model the SE solar cells with varying the sheet resistance from 70 to $170 \Omega/\square$ in the illuminated area, because high sheet resistance is beneficial to both Auger recombination reduction and surface passivation. In the simulation, the surface recombination rate as the function of sheet resistance was set referring to Ref. [24]. Fig. 7 depicts the PC1D calculated (together with the measured) EQEs for the SE solar cells with different sheet resistances in the illuminated area. We note that the PC1D calculated EQE curve matches well with the measured EQE for the cell with a sheet resistance of 70 Ω/\Box , except in the wavelength range of less than 350 nm where the incident light encounters a heavy absorption in SiN_x laver, which is neglected by PC1D. Moreover, the PC1D calculated electrical parameters of the SE and reference solar cells, listed in Table 1, are almost identical to the corresponding average values of the experimental data. These indicate that our simulation results by PC1D are convincible. When the sheet resistance in the illuminated area of the SE solar cells is enhanced from 70 to 170 Ω/\Box , both V_{OC} and J_{SC} increase (see Table 1) due to the reduced Auger and surface recombination. Simultaneously, according to $R_{ds} = \rho_s b^2 / 12$ [25], with R_{ds} the series resistance, ρ_s the sheet resistance, and b the gridline spacing, the increase of series resistance is calculated to be 0.167 and $0.333 \,\Omega \,\mathrm{cm}^2$ for the 120 and $170 \,\Omega/\square$ SE cells with respect to the 70 Ω/\Box SE cells. As a result, the FF decreases from 79.55% to 78.80% for the 120 Ω / \Box SE cells and to 77.97% for the 170 Ω / \Box SE cells. Overall, the 170 Ω/\Box SE solar cells do not perform better than the 70 Ω/\Box SE solar cells in terms of η , as a compromise between the improvement of V_{OC} , J_{SC} and strong decrease of FF. Nevertheless, for the 120 Ω/\Box SE solar cells, the improvements of V_{OC} and J_{SC} exceed the degeneration of FF. Thereby higher η (19.13%) can be achieved. Here, it is worth mentioning that some ink technologies have the disadvantage that dopant moves around in the furnace, and it is hard to achieve light doping ($\geq 120 \Omega/\Box$) in the illuminated area. However, for our phosphorus ink technology, by controlling the property of the nanosilicon dioxide, the spreading of dopant is effectively controlled. With the aid of four-point probe, we have found that the sheet resistance of the region outside the ink pattern is higher than 170 Ω/\Box when no POCl₃ is additionally used as dopant source. Therefore, the target of 120 Ω/\Box can be realized with appropriate POCl₃.

4. Conclusion

We have developed very cheap phosphorus ink as a novel material to manufacture SE crystalline silicon solar cells. The phosphorus ink exhibits colorless, and its viscosity is high enough to keep its screen printed pattern. After drying process, only C, O, Si and P elements are residual. We have successfully applied the simple phosphorus ink technology to large batches fabrication of SE silicon solar cells, achieving an average η of 19.01% (peak η of 19.27%) on commercialgrade Cz silicon wafers with a good yield of 99.58%, small standard deviation of η (0.11%), and low fragmentation rate of 0.09%. Compared to the homogeneous emitter counterparts, the SE solar cells have higher V_{OC} and I_{SC} due to the reduced Auger and surface recombination. Moreover, the performance of the SE solar cells exhibits narrow distribution which is beneficial to reduce the cells fabrication cost. Due to the heavy doping and deep junction under the contact area, all the FFs of the SE solar cells exceed 79.5%, showing an advantage of being independent of the type of silver paste, which provides another opportunity to further reduce the cells fabrication cost. Through the modeling by PC1D, we have shown that the performance of our SE silicon solar cells can be further improved by increasing the sheet resistance to $120 \Omega/\Box$ in the illuminated area. In conclusion, we believe that the phosphorus ink technology offers a simple, costeffective and reliable approach to realize high efficiency SE silicon solar cells. In fact, the phosphorus ink SE technology has been successfully employed in full capacity of 5 production lines in a local photovoltaic company since June, 2012.

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