Hitachi Chemical
Working On Wonders

Doping Paste for Photovoltaic Solar Cell

Takeshi Nojiri
New Business Development Headquarters
Tsukuba Research Laboratory

Mitsunori Iwamuro
Advanced Performance Materials Operational Headquarters
Advanced Integrated Materials Business Sector
Advanced Paste R&D Department

1 Abstract

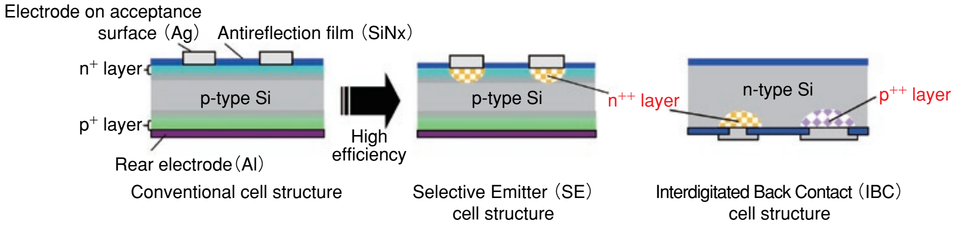
In response to global trends such as environmental protection and abolition of nuclear power plants, renewable energy sources have attracted attention increasingly[1]. Especially photovoltaic (PV) related business has been expected as a growth industry. In the field of the crystalline silicon PV, the development of high performance cells of new structure such as the selective emitter cell, back-contact cell and bifacial cell has been progressing quickly. We paid our attention to the doping of phosphorus (P) or boron (B) indispensable to these cells. In this paper, we outlined the development of doping paste (DP) which can diffuse P or B into silicon uniformly and selectively.

2 Features of Developed Product

- Uniform diffusion of dopant (phosphorus or boron) under Si surface increases the uniformity of sheet resistance in the substrate.
- The performance of dopant diffusion on the area coated with this product (selective diffusion) is high.
- Solubility in hydrofluoric acid is high, and remnants of the hydrofluoric acid etching process are minimized.

3 Background of Development

Figure 1 shows a cross-sectional view of a conventional PV cell and the high-efficiency PV cell (SE and IBC cells). We analyzed PV cell structure trends, and noted that the n-type doping paste was suitable for forming the n^{++} layer of SE cell, and also applicable to the formation of p^{++} and n^{++} layers of IBC by combining p- and n-type doping pastes. In the feasibility study of doping paste, which started in the second half of 2009, we selected phosphorus and boron-mixed compounds, and after confirming the potential for dopant diffusion with these compounds in principle, started the full-scale development of doping paste.



Conventional cell structure　Selective Emitter（SE） cell structure　Interdigitated Back Contact（IBC） cell structure

Figure 1 Cross sectional view of the conventional cell and the next generation cell

4 Details of Technology

(1) Material design concept

Figure 2 shows the process of forming the n^{++} layer using the developed n-type doping paste, which consists of phosphorus mixed compound, resin and solvent. When the paste is coated on the Si substrate, and the resin and solvent are removed in the drying and degreasing process, only phosphorus-mixed compound remains as particles. As the latter is designed to melt at a high temperature over 800°C, and follow the Si surface at the diffusion temperature (≧800°C), phosphorus diffusion on the Si surface is uniform. The same design concept is used for p-type doping paste, namely, boron-mixed compound is used in material design to

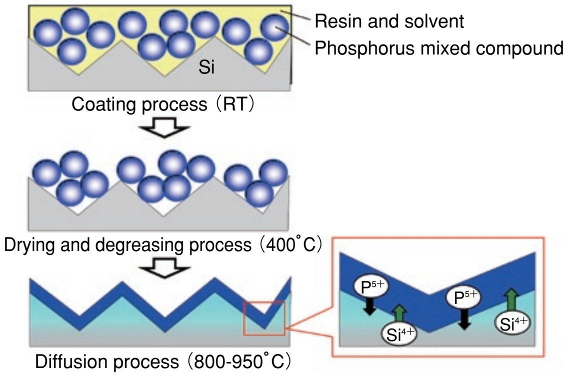


Figure 2 Concept of n^{++} layer forming on Si with n-type doping paste

facilitate the uniform diffusion of boron.

(2) Evaluation of p-type doping paste

According to the aforementioned material design concept, **Figure 3** shows the results of measurement and mapping of the sheet resistance of boron doped Si surface (156 mm x 156 mm, entire size) using the p-type doping paste containing boron-mixed compound. The colors indicating the sheet resistance values are homogeneous in the surface area, confirming the uniform diffusion of boron on the Si surface. **Figure 4** shows the SEM image of boron doped Si surface after etching with hydrofluoric acid, clearly showing no residual boron-mixed compound. Diffusion of gases such as BBr_3 is a typical way of boron doping, but this generates residual material due to the boron-rich layer (BRL) during diffusion, impairing efficiency.[2)] The SEM observation of this product does not find any residual, and confirms repellency to indicate the absence of BRL. This means the p-type doping paste will be effective for forming the p layer of various high-efficient cells.

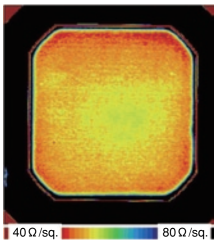


Figure 3 Sheet resistance mapping on the boron-doped Si surface with p-type doping paste

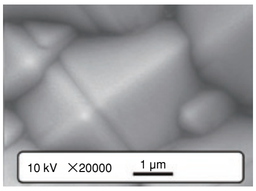


Figure 4 SEM image of the boron doped Si surface after etching with HF solution

(3) Evaluation of n-type doping paste

Figure 5 shows the result of SIMS analysis of phosphorus diffusion in dosed and non-dosed areas 2 mm apart from the dosed area, beneath the Si surface dosed and diffused with n-type doping paste in a pattern. The phosphorus concentration in the non-dosed area near the Si surface is significantly low, although high in the dosed area, indicating the area is sufficiently dosed and confirming a highly selective diffusion of phosphorus. Using this selective diffusion, we made the prototype SE cell shown in Figure 1, and evaluated its PV properties. **Table 1** shows the results. The SE cell using our n-type doping paste has greater short-circuit current density (Jsc) and open-circuit voltage (Voc) than those of conventional cells, resulting in an increase of 0.4% in conversion efficiency (Eff). This product was marketed as YT-2100-N in the first half of 2012, and is used by PV manufacturers for SE.

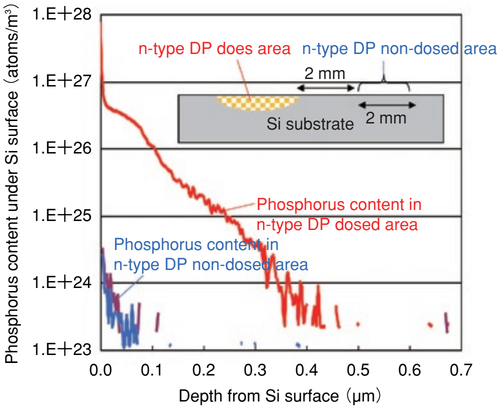


Figure 5 Concentration distribution of Phosphorus beneath Si surface doped with n-type doping paste [SIMS analysis]

Table 1 PV Properties of Selective Emitter Cell doped with n-type Doping Paste

Cell type (single crystal Si)	Short-circuit current density (Jsc) [mA/cm²]	Open-circuit voltage (Voc) [mV]	Fill factor (F.F.)	Conversion efficiency (Eff) [%]
Conventional cell	37.0	623	80.1	18.5
SE cell	**37.4**	**634**	**79.7**	**18.9(+0.4)**

5 Future Prospects

- Development of p-and n-type doping pastes for the IBC cell
- Identification of the doping paste composition available for simultaneous diffusion of phosphorus and boron

【References】

1) Present Situation and Future Prospect of PV Technologies and Market 2013, Fuji Keizai Group (2013)
2) M. A. Kessler et al.: Semiconductor Science and Technology, 25 (2010) 055001 (9pp)

【Related Patents】

Japan Patent Nos. 04868079, 04978759, 05176158, and 05176159