INKJET SOLUTION FOR DIRECT PRINTING OF LOCAL DIFFUSION BARRIERS ON SOLAR CELLS

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ABSTRACT: The realization of high-efficiency silicon solar cell designs like rear contacts, local back surface fields or selective emitters in industrial solar cell production, depends on the existence of cost-effecitve processing techniques. This report introduces the inkjet-ready Isishape SolarResist^{TM} diffusion barrier solution. It can be used to directly print diffusion barrier layers for the local formation of highly-doped regions without additional structuring. Thin films of 190 nm thickness work as a barrier against industrially relevant phosphorus diffusions. No adverse effect on the charge carrier lifetime is observed. Printed line widths of 90 µm are achieved, and the minimum gap width between lines is 50 µm.

Keywords: Diffusion Barrier, Inkjet, Diffusion, Doping

1 INTRODUCTION

High-efficiency silicon solar cell designs like rear-contacted cells,[1] PERL (passivated emitter and rear locally diffused) cells,[2] or cells with a selective emitter, feature highly boron- or phosphorus-doped regions on only a part of the cell area. Such locally doped areas are usually created by applying laterally structured diffusion barrier layers before a high-temperature diffusion process.

Diffusion barriers currently deployed are thermally grown silicon oxides as well as silicon nitride, silicon dioxide or silicon carbide layers formed e.g. by plasma enhanced chemical vapour deposition. However, these barrier layers have to be structured after their full-area deposition by e.g. laser ablation or lithography. Therefore, several process steps are necessary to obtain the desired local protection of the wafer against a following diffusion process.

In this work, we present Merck's Isishape SolarResist^{TM} silicon dioxide-based barrier solution which is the first diffusion barrier to be locally applied by inkjet printing. The direct deposition by inkjet printing with high lateral resolution avoids any additional structuring, thus providing a simple, reproducible process. No intermediate stages like the fabrication of printing screens are needed. Furthermore, this contactless method avoids any mechanical stress on the wafer. Thus inkjet printing of Isishape SolarResist^{TM} can be applied to very thin or brittle wafers in solar cell production.

We demonstrate the suitability of Isishape SolarResist^{TM} for solar cell production by presenting the topographic properties and the lateral resolution of printed patterns for typical surface conditions of silicon wafers. The barrier function in a typical phosphorus diffusion process is shown, as well as the negligible impact on the charge carrier lifetime.

2 EXPERIMENTAL

2.1 Inkjet setup

Ink Jet (IJ) printing is well known in desktop and graphic arts printing and has increasingly moved into industrial printing, patterning and related manufacturing applications as exemplified by processes ranging from textile printing to the fabrication of colour filters for flat panel displays.[3,4] Piezo drop on demand (DOD) IJ is the most frequently adopted head technology, relying on piezo crystal deformation to create a pressure wave within an IJ nozzle and eject single drops on demand.[5]

We have selected the FujiFilm Dimatix 2800 DMP printer system featuring a 16 nozzles DOD printhead with drive-per-nozzle (DPN) for initial and rapid development of the Isishape SolarResist^{TM} ink, and the FujiFilm Dimatix SX3 DOD head (128 nozzles head with DPN) mounted on a Litrex 70L system, for industrial demonstration.[6,7]

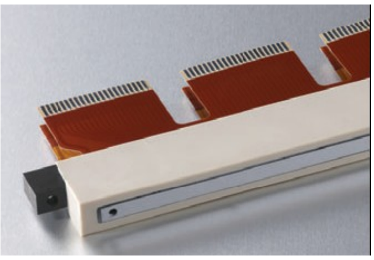


Figure 1: FujiFilm Dimatix SX3 DOD head with 128 nozzles placed in one row on the lower side.

The DPN technology allows to individually fine tune the performance of each nozzle with respect to ejection drop velocity and drop volume in their head array. The FujiFilm Dimatix SX3 head shown in Figure 1 is a an optimized version of the original SE head, showing increased chemical resistance to functional fluids, decreased drop size of 12 pl, and improved accuracy of drop firing to produce high-quality reproducible patterns.

2.2 Sample preparation and characterization techniques

The optimization of substrate pre-treatment, composition of the ink, and printing parameters for minimum feature size, has been carried out on single crystalline silicon wafers with different surface conditions: polished, shiny etched, as-cut and alkaline damage-etched, and finally alkaline textured. The geometry analysis of the printed patterns is done by using an optical microscopy, a scanning electron microscope (SEM) and a pin profiler (DekTak).

For the determination of (1) the charge carrier lifetime after phosphorus-diffusion and (2) the barrier function, we used *p*-type FZ-silicon wafers with a specific resistivity of 200 Ωcm. A 3.0×1.5 cm large area of the wafers is covered with a closed Isishape SolarResist^{TM} film. The samples are annealed at 350°C for 15 min, before they undergo a phosphorus diffusion process in a tube furnace with process temperature 900°C, 20 min $POCl_3$ flow, and 20 min drive-in without $POCl_3$. The resulting sheet resistance on wafers not covered with Isishape SolarResist^{TM} is 40 Ω/square. After phosphorus diffusion, the Isishape SolarResist^{TM} film is removed in diluted hydrofluoric acid.

The depth-resolved dopant profile within and outside the Isishape SolarResist^{TM}-covered region is then obtained from electrochemical capacitance-voltage profiling.[8] The spatially resolved charge carrier lifetime is deduced from microwave-detected photoconductivity (MWPCD) measurements, of samples that are covered by a 70 nm thick SiN_x layer with a refractive index of $n = 2.4$. The SiN_x layer is deposited by the plasma enhanced chemical vapour deposition (PECVD) technique.

3 RESULTS AND DISCUSSION

3.1 Substrate pre-treatment

We find that a hydrophilic wafer surface allows for the best film uniformity. An effective process has been identified for a reproducible surface pre-treatment by chemical oxidation: We clean the wafers for 15 min in RCA-1 (15% H_2O_2 and 15% NH_4OH in water), followed by a 1 min dip in 1% aqueous hydrofluoric acid to remove the silicon oxide, and the chemical oxidation for again 15 min in RCA-1 solution. Finally the wafers are rinsed deionised water and dried in nitrogen.

3.2 Design of the Isishape SolarResist^{TM} Ink

Functional products for inkjet deposition processes need to fulfil two basic requirements: They have to be printed reliably with the desired resolution, and the physical properties of the printed film must allow for the desired function. Isishape SolarResist^{TM} ink has been designed to meet these requirements by selecting our soluble barrier chemistry with low hazard potential and provide flexibility to adjust many formulation parameters to meet both jetting and application requirements.

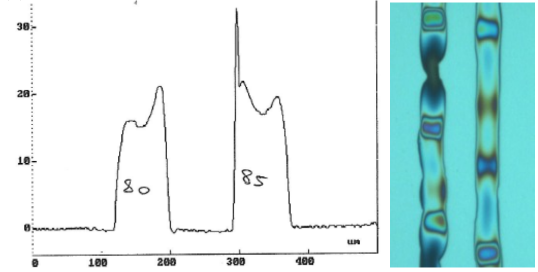
Matching viscosity, surface tension and chemical compatibility of the ink to the requirements of the selected inkjet head is critical to successful and reproducible jetting. Development of Isishape SolarResist^{TM}, has resulted in an ink whose principal carrier solvent is toxicologically and environmentally benign, providing an ink viscosity and surface tension in the optimum range of 7-12 cps and 30-33 dyne cm^{-1}. The ink has a suitable high boiling point so that it does not dry out in the inkjet nozzles, which would result in malfunctions.

Excellent drop formation is observed from both the rapid development DMP head and the industrial SX3 head. All 128 nozzles fire within the specified drop velocity tolerance of 4.5 m/s (± 2%) after optimization of the drive waveform.

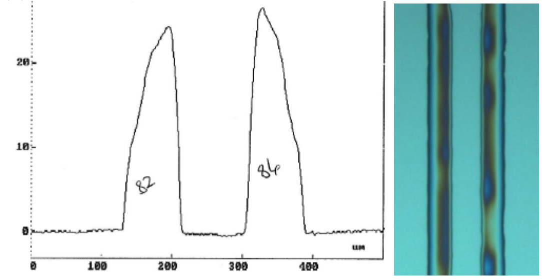
3.3 Substrate temperature

Achieving the highest image quality with the correct film thickness relies on optimisation of Isishape SolarResist^{TM} with respect to drop placement pattern and substrate temperature. Ink formulation and substrate temperature have to be carefully adjusted for optimum wetting of substrate surface: Ink droplets ejected from the printhead nozzle rapidly spread upon landing on the substrate as controlled by the surface tension and surface energy, with the movement being finally arrested by solvent evaporation.

(a) $T_{substrate} = 60°C$



(b) $T_{substrate} = 90°C$



(c) $T_{substrate} = 140°C$

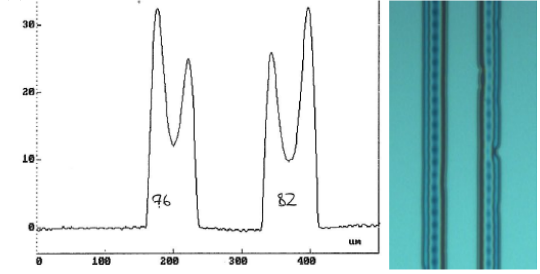


Figure 2: Height profiles measured with the pin profiler, and microscope images of Isishape SolarResist^{TM} lines printed on polished wafers for different wafer temperatures. The best uniformity is obtained with $T_{substrate} = 90°C$.

Figure 2 shows height profiles and optical microscope images of lines printed with the Dimatix 2800 DMP system on polished wafers, at different temperatures $T_{substrate} = (60, 90, 140)°C$. Printing Isishape SolarResist^{TM} on wafers at less than 80°C results in de-wetting of the ink prior carrier solvent evaporation and unacceptable image quality while printing at above 120°C results in excessive ‘coffee staining’, where the edge is much thicker than in the middle.[9] The optimum wafer temperature is 90°C, allowing for a film thickness around 220 nm.

3.4 Printing with high lateral resolution

Resolution is controlled by the mechanical accuracy of the printer, drop size, ink spread prior to drying and the substrate surface. In order to further optimize Isishape SolarResist$^{\mathrm{TM}}$ for a high image quality with high lateral resolution, we transferred the results shown in Sections 3.2 and 3.3 to our Litrex system with SX3 printhead. A 12 pl drop typically ejected from the SX3 head has a diameter in flight of 29 microns.

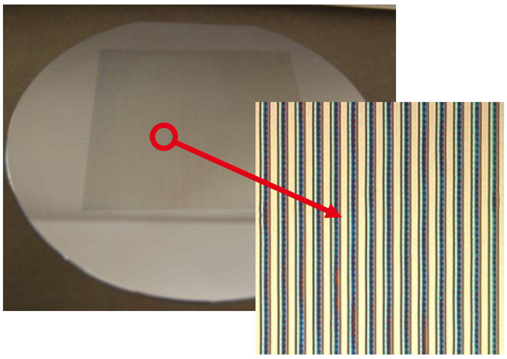


Figure 3: Polished silicon wafer with 90 µm lines and 50 µm gaps pattern printed on the Litrex system.

An optimised line width of 90 µm can be obtained with Isishape SolarResist$^{\mathrm{TM}}$ on polished and shiny etched wafers when multiple drops are used to form lines with the desired dry film thickness of >150 nm. Gaps between lines can be made smaller and are limited by surface roughness. The roughness of damage-etched and textured wafers result in some line spreading, however their roughness prohibits quantification by a pin profiler. Holes in printed big blocks of Isishape SolarResist$^{\mathrm{TM}}$ can be obtained with feature sized down to 65 micron. Figure 3 shows a full wafer with 90 µm lines and 50 µm gaps pattern printed on the Litrex system.

Figure 4 shows the cross-sectional SEM image of the edge of an inkjet-printed line on a polished Si wafer. The full thickness of the line reduces within 5 µm to zero. Thus only in this narrow stripe of 5 µm dopant atoms might penetrate the barrier layer.

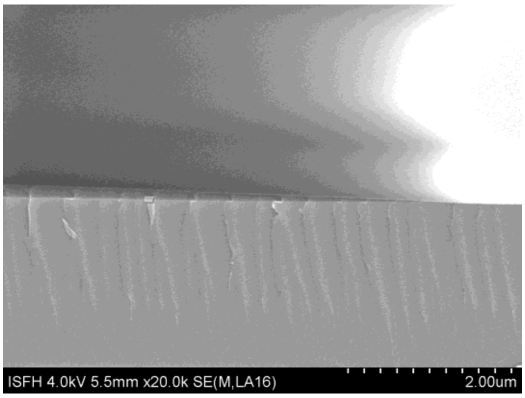


Figure 4: Edge region of an inkjet-printed Isishape SolarResist$^{\mathrm{TM}}$ line. Spreading is only (5…6) µm.

3.4 Barrier function

Inkjet-deposition of Isishape SolarResist$^{\mathrm{TM}}$ with optimized parameters as shown in Sections 3.2 and 3.3, currently results in a film thickness of about 190 nm. In order to prove the functionality of such films as diffusion barriers, we prepare two types of samples from 200 Ωcm *p*-type Si wafers: On the first type, narrow lines with a width of 100 µm with 100 µm-wide gaps are deposited by inkjet printing, similar to the ones shown in Figure 3. These samples are used for laterally resolved SEM measurements. On the second type of samples, an area of 3.0 cm by 1.5 cm is completely covered with Isishape SolarResistTM. These samples are used for measurements of the depth-resolved dopant profiles by the ECV method. The applied diffusion process results in an emitter with a sheet resistance of 40 Ω/square on non-protected wafers.

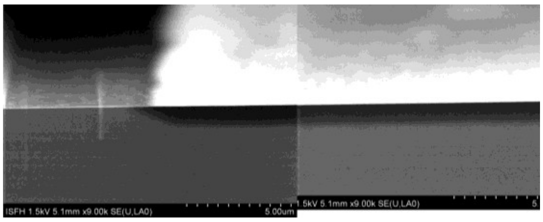


Figure 5: Side-view SEM image of the cross-section of a partially Isishape SolarResist$^{\mathrm{TM}}$-covered *p*-type Si wafer *after* phosphorus diffusion and removal of the barrier layer. The dark contrast at the cleaved edge of the non-protected right-hand part indicates *n*-type doping due to the diffusion of phosphorus atoms. The left-hand part was protected by a 190 nm thick Isishape SolarResist$^{\mathrm{TM}}$ layer. The bright contrast there indicates that no phosphorus has penetrated the wafer.

Figure 5 shows an SEM image of the cross-section of a sample of the first type. The left part of the sample was covered by a Isishape SolarResist$^{\mathrm{TM}}$ line during phosphorus diffusion, while the right part represents a gap between two lines. The dark contrast at the cleaved edge of the non-protected right-hand part indicates *n*-type doping due to the diffusion of phosphorus atoms. The left-hand part was protected by a 190 nm thick Isishape SolarResist$^{\mathrm{TM}}$ layer. The bright contrast there indicates that no phosphorus has penetrated the wafer.

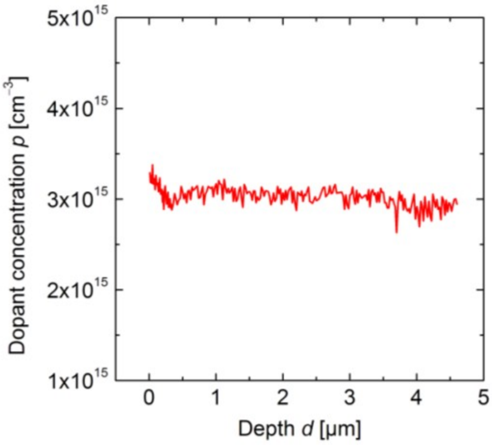


Figure 6: Depth-resolved dopant profile obtained from ECV measurement within a Isishape SolarResist$^{\mathrm{TM}}$-protected area of a 200 Ωcm *p*-type Si wafer, after phosphorus-diffusion. Only the background doping of the substrate can be detected. The applied diffusion process results in an emitter with a sheet resistance of 40 Ω/square on non-protected wafers.

Figure 6 shows the depth-resolved dopant profile obtained from ECV measurement within a Isishape SolarResist^{TM}-protected area of a 200 Ωcm *p*-type Si wafer, after phosphorus-diffusion. Only the background doping of the substrate can be detected. These results show that locally applied, 190 nm thick films of Isishape SolarResist^{TM} provide protection of silicon wafers against industrially relevant phosphorus diffusion processes.

3.5 Bulk lifetime

Besides its barrier function and ability to be printed with high resolution, the applicability of Isishape SolarResist^{TM} to solar cell manufacturing also depends on its potential to allow for high charge carrier lifetimes. Therefore it is essential that Isishape SolarResist is free of contaminants that might form recombination centers in the crystalline silicon bulk during high-temperature diffusion processes.

The passivation of partially Isishape SolarResist^{TM}-protected Si wafers by PECVD-deposited SiN_x after diffusion, is a sensitive method to detect any effect of Isishape SolarResist^{TM} on the bulk carrier lifetime. Comparison of the bulk carrier lifetime in covered and non-covered areas would reveal potential contaminations, particularly by highly mobile cations that would diffuse into the silicon bulk material and form recombination centers there. The absence of such cationic (metallic) contaminations is the one most important prerequisites for high-temperature processes.

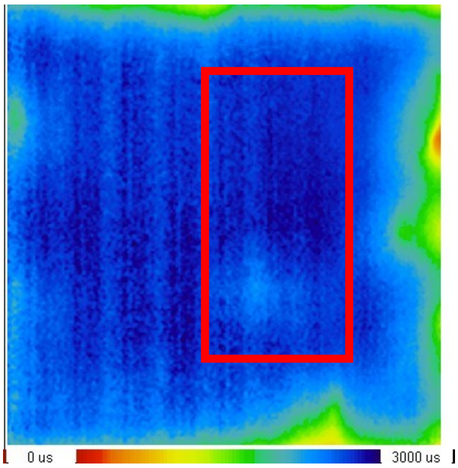


Figure 7: Spatially resolved measurement of the effective charge carrier lifetime of a 200 Ωcm *p*-type Si wafer after protection by Isishape SolarResist^{TM}, phosphorus diffusion, removal of the emitter, and surface passivation by SiN_x. The red rectangle shows the area that was protected by Isishape SolarResist^{TM}. No effect of Isishape SolarResist^{TM} on the bulk carrier lifetime is discernible.

Figure 7 shows the spatially resolved carrier lifetime of a 200 Ωcm *p*-type Si wafer after protection by Isishape SolarResist^{TM}, phosphorus diffusion, removal of the emitter, and surface passivation by SiN_x. The red rectangle shows the area that was protected by Isishape SolarResist^{TM}. No effect of Isishape SolarResist^{TM} on the carrier lifetime is discernible. The mean effective carrier lifetime is $\tau_{eff} = (2700 \pm 100)\ \mu s$ in both, covered and non-covered areas.

We calculate the bulk carrier diffusion length $L_{bulk} = (4.5 \pm 1)$ mm from

$$\frac{1}{\tau_{eff}} = \frac{D}{L_{bulk}^2} + \frac{2S}{W}, \qquad (1)$$

where $D = 34.3\ cm^2/s$ is the diffusion constant, $W = 300\ \mu m$ is the thickness of wafer, and $S = (3 \pm 1)$ cm/s is the recombination velocity of the SiNx-passivated surfaces, as deduced from lifetime measurements on reference wafers without diffusion and without Isishape SolarResist^{TM}.

The obtained value of the bulk carrier diffusion length is very close to the intrinsic value of 6.7 mm as calculated from the parameterization by Kerr and Cuevas.[10] We therefore conclude that Isishape SolarResist^{TM} is free of contaminants that could affect the bulk quality of solar cells in high-temperature diffusion processes.

4 SUMMARY

Merck established the silicon dioxide-based Isishape SolarResist^{TM} diffusion barrier solution that is designed for direct inkjet printing. This direct application method provides high lateral resolution with currently achievable line widths of 90 µm, and gap widths of 50 µm. The barrier function of such lines has been shown, as well as the absence of any effect on the charge carrier diffusion length of high-quality FZ-Si wafers.

We give evidence on an “easy to use” application procedure enabling the user to realize designs like e.g. back-contacted solar cells, local back surface fields, or selective emitters.

5 ACKNOWLEDGEMENTS

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