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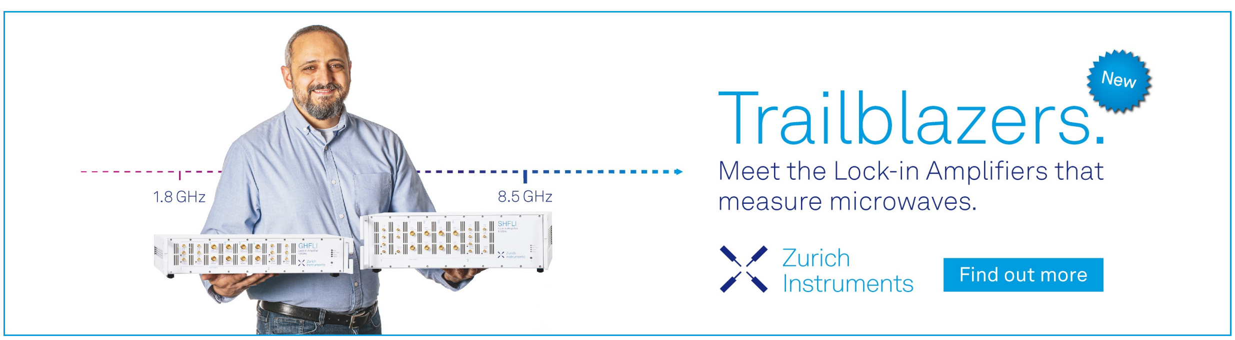

Inkjet- and FlexTrail-printing of Silicon Polymer-based Inks for Local Passivating Contacts

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Abstract. In this work innovative additive printing methods for formation of polycrystalline silicon (poly-Si) and polycrystalline silicon carbide (poly-SiC) layers of local tunnel oxide passivating contacts (TOPCon) is evaluated. Replacement of conventional vacuum processes and vapor-phase deposition by additive printing of Si in fabrication process of high efficiency solar cells reduces processing complexity, and, hence manufacturing costs. Reliable inkjet- and FlexTrail-printing processes are developed for liquid-phase polysilane and organic polysilazane inks that are precursors of Si and SiC, respectively. FlexTrail is introduced as a potential technology to print uniform closed thin films of polysilane free of ruptures. Moreover, from inkjet-printing of the developed polysilane ink, homogenous, closed and crack free thin films of poly-Si are obtained after high temperature annealing. The polysilane ink is formulated considering evaluation of several solvents and photoinduced polymerization conditions. Inkjet-printing process development and optimization according to high frequency rheological characterization of organic polysilazane (OPSZ) is presented. Printed thin films are characterized after high temperature annealing (T = 950 °C, t = 60 min) to be uniform and free of micro cracks.

INTRODUCTION

Si is entrenched as a necessity in the Si photovoltaic (PV) and electronics industry. However, only solid, and gaseous states of Si have been utilized in fabrication processes of Si PV and electronic devices. Several research groups around the world are conducting studies on liquid Si and its application methods on different substrates, such as Si wafer [1–7]. However, it has never been applied industrially. We have pursued the development of novel application methods of liquid precursors of Si and SiC, such as industrially compatible inkjet- and innovative FlexTrail-printing. FlexTrail-printing has been introduced as a novel printing technology at Fraunhofer ISE with significantly higher process stability compared to inkjet [8]. The inherent characteristic of FlexTrail-printing enables interruption-free ink application as well as high tolerance toward rheology of inks and process temperature. Replacement of traditional vacuum deposition for fabricating Si or SiC thin films and photolithography processes with additive printing can significantly simplify the process sequence. Thus, reducing manufacturing cost of e.g. local passivating contacts structures for both-side and single-side contacted silicon solar cells. This can lead to the creation of a new field of printed Si PV and electronics.

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In this work, liquid polysilane formulated from cyclopentasilane (CPS) and OPSZ inks were printed for formation of Si and SiC thin films, respectively. Rheological properties of OPSZ, such as complex viscosity and elasticity that are determinative parameters in inkjet printing process development were characterized. FlexTrail, however enables high tolerance towards rheology of inks due to its inherent characteristics.

We demonstrate the deposition of homogenous, closed, and defect-free thin-films of poly-Si and poly-SiC utilizing inkjet- and FlexTrail- printing. This is of great importance specially for printing of Si precursor (liquid polysilane) as instability and rupture formation of polysilane liquid film has been recognized as a bottleneck for fast progress of this field. Possible origin of the issue and potential solutions to tackle it, have been addressed in several studies, such as [1, 4, 9].

EXPERIMENTAL DETAILS

Samples were realized on (100) oriented phosphorous-doped *n*-type float-zone (FZ) silicon wafers with a specific resistivity of 1 Ωcm and a thickness of 200 µm. To this end, wafers were cleaned according to Radio Corporative of America (RCA) standard clean procedure. An ultra-thin silicon oxide (SiO_x) layer (approximately 1.3 nm) was thermally grown in a tube furnace at 600 °C for 10 minutes on both sides. Subsequently, CPS and OPSZ inks were inkjet- or FlexTrail-printed on one side of wafers. A "PiXDRO LP50" from Suss MicroTech was utilized in this work. After printing, samples were cured thermally on a hotplate or using an ultraviolet (UV) light source. Finally, samples were introduced into a tube furnace for high temperature annealing. All steps of the experiments were carried in a glovebox under nitrogen atmosphere.

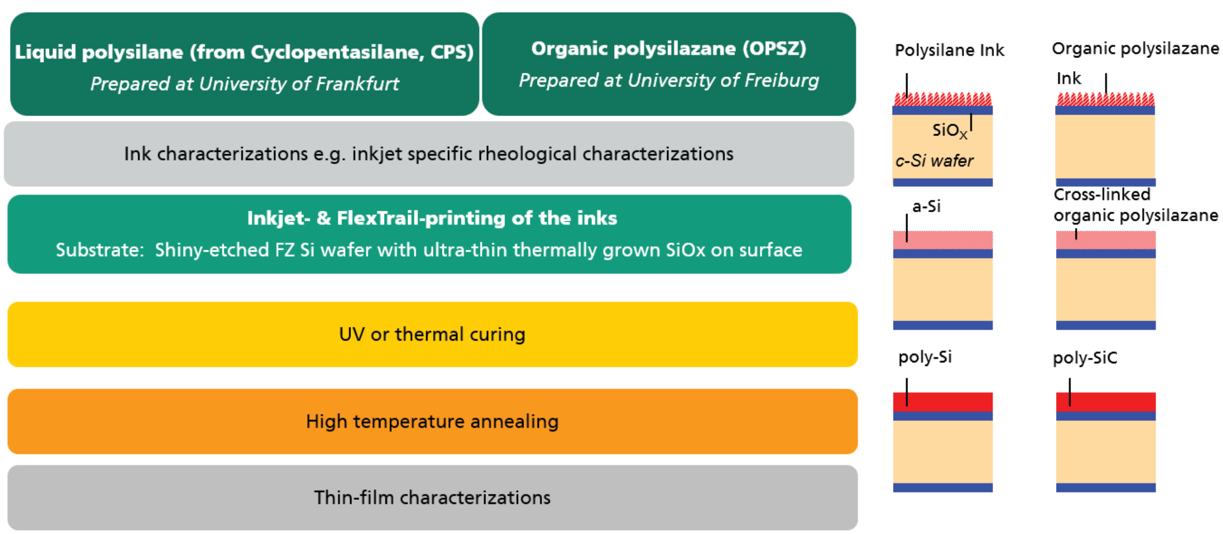


FIGURE 1. Process sequence and schematic visualization of sample preparation for evaluation of Inkjet- and FlexTrail-printing process developments and characterizations.

Printing of Polysilane and OPSZ Inks

The utilized precursor of polysilane in this work is CPS. The polysilane ink formulation and photoinduced ring-opening polymerization condition were evaluated to obtain stable jetting of nozzles and at the same time avoiding rupture formation in the printed films. To improve jetting stability, selected solvents were degassed prior to inkjet printing. Moreover, towards optimized inkjet printing of polysilane, printing parameters, such as temperature (printhead and substrate), pressure waveform (time dependent voltage at piezo element) and printing speed were investigated. Ideal inkjet-printing behavior implies minimum nozzle clogging, absence of satellites, tails, ligaments, homogeneous and precise deposition of ink over the substrate.

The "PiXDRO LP50" inkjet printer allows application of cartridge-based printheads, herein we utilized a custom-made ink reservoir for the cartridge which requires only less than ~50 µl of ink for jet priming. The printed films were cured on a hotplate at 400 °C for 30 min for thermal decomposition of polysilane into a-Si.

The rheology of inks plays a significant role in the inkjet printing performance. Thus, it is beneficial to characterize rheological behavior of the inks at certain inkjet operating points. The eventual success in obtaining desired inkjet-printing processes is determined, to a large extent, by viscoelastic behavior of the inks. Indeed, rheological properties (viscoelasticity) of polymer-based inks determine their behavior in response to the stimulus of shear strain (frequency) which is applied through the piezoelectric elements at the nozzles of the inkjet printer [10].

In this work, complex viscosity, and viscoelasticity of OPSZ were characterized using a Piezo Axial Vibrator (PAV) rheometer. The rheometer can be used to investigate viscoelastic behavior and jettability of inks in a frequency range of f = 1 Hz - 10 kHz, which covers the operating conditions of the printhead of an inkjet printer even in industrial scale. The OPSZ inks utilized in this work were formulated at university of Freiburg.

RESULTS

In this section experimental results from rheological characterization, inkjet- and FlexTrail-printing of the inks are presented.

Rheology

Figure 2 illustrates rheological characterization of the OPSZ ink with the TriPAV rheometer. It shows that at ink temperature of 25 °C, the complex viscosity is only slightly dependent on the frequency (~26 mPas). The elastic modulus of OPSZ at ink temperatures of 25 °C, 40 °C, and 50 °C starts to be effective at frequencies between 100 to 1 kHz with an increasing trend by frequency. Elasticity decreases by increasing the ink temperature. The smallest value at 1 kHz realized at 50 °C to be 8 Pa. However, it is 80 Pa at 25 °C at the same frequency. It could be seen in Fig. 2 that the OPSZ ink used in this work is mainly Newtonian up to high frequencies. A stable inkjet process could be achieved by setting print head's temperature to 50 °C and adjusting firing frequency and timing of the pressure waveform to make the elastic modulus less effective.

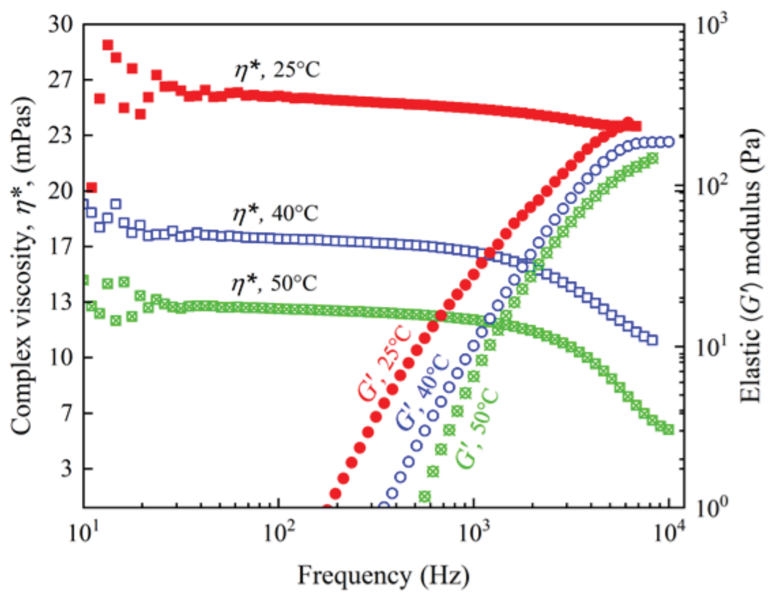


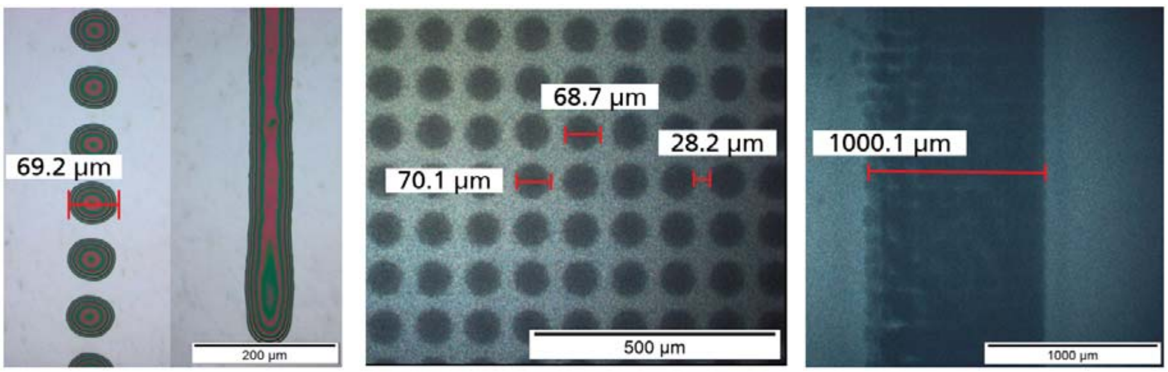
FIGURE 2. Complex viscosity (η^*) and elastic modulus (G') of OPSZ with respect to frequency measured at 25 °C, 40 °C and 50°C utilizing TriPAV rheometer.

Inkjet-printing

Polysilane

Figure 3 illustrate droplets, line, and area of inkjet-printed polysilane ink on flat shiny etched (Fig. 3 (a)) and textured (random pyramids) (Fig. 3 (b) and (c)) surface of Si wafer after conversion into a-Si (T_{hotplate}= 400 °C, t_{hotplate}

= 30 min). According to [2] polysilane decomposes into a-Si at annealing temperatures above 360 °C. The ink formulated by solving 25 vol.% CPS in 75 vol. % solvent. Cyclooctane and dodecane were our choices among several evaluated solvents due to their compatibility with CPS and proper drying speed. UV polymerization of the ink prior to printing of the presented results carried out using a light source with power of 3.5 watt and wavelength of 365 nm. The ink was exposed to the light source from distance of 30 cm (perpendicular) for 40 to 60 s. UV polymerization conditions should be adjusted according to each polysilane ink formulation. Results of Fig. 3 obtained by printing on a heated substrate $T_{\text{substrate}}$= 90 °C, which significantly improved stabilizing printed liquid polysilane on the substrate. Figure 3 shows that feature size of ~70 µm could be obtained on both shiny etched and textured surfaces using a nominal drop volume of 10 pl, printing resolution of 100 x 100 dpi, and printing speed of 150 mm/s. Moreover, uniform distribution of droplets over the substrate confirms stability and precision of our printing process. The printed area of Fig. 3 (b), illustrating a closed thin film was created with the same printing speed and increasing printing resolution to 300 x 300 dpi.



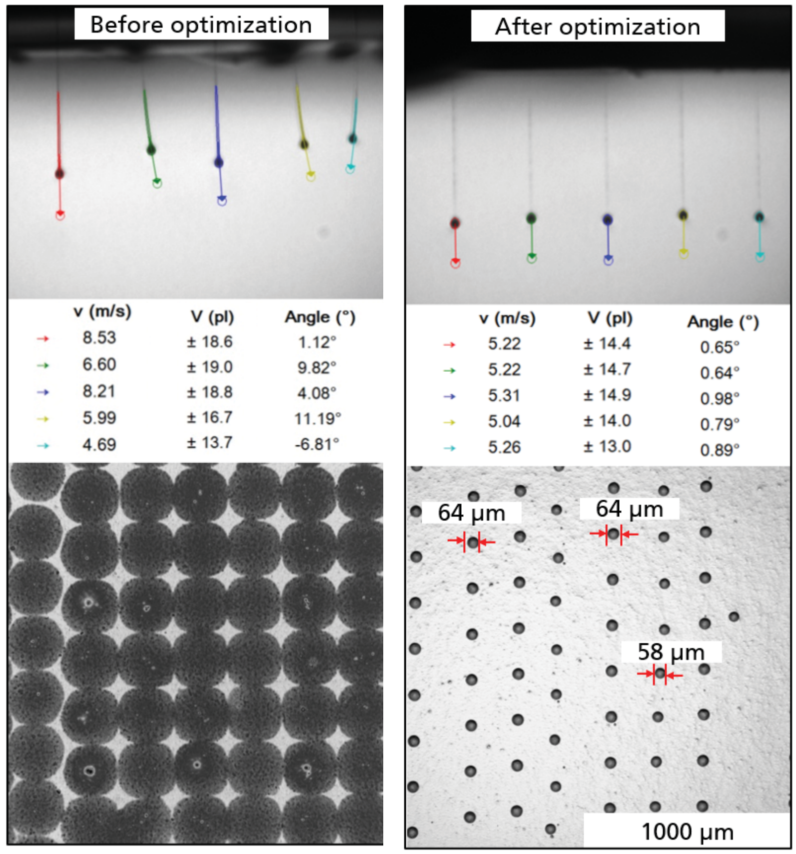
(a) (b) (c)

FIGURE 3. Optical microscope image of printed polysilane ink (a) droplets and line on a shiny etched surface, (b) and (c) droplets and area, respectively, on a textured surface of Si wafer after its conversion into a-Si on a hotplate (T_{hotplate}= 400 °C, t_{hotplate} = 30 min).

OPSZ

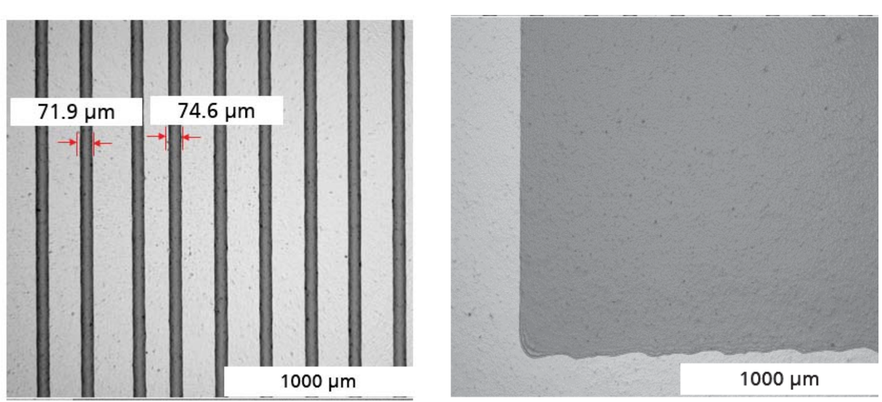
Figure 4 (a) shows jetted droplets of OPSZ in flight and on the substrate (flat shiny etched surface of Si wafer) obtained from non-optimized inkjet-printing process, in which a high actuation voltage was applied on piezo elements for droplet formation of viscos OPSZ. We optimized our printing parameters according to rheological characterization of OPSZ presented in Fig. 2. Setting the printhead temperature to 50 °C tuned viscosity of the ink to be in suitable range of inkjet printing and reduced elastic modulus which had a remarkable effect on obtaining stable and precise print. Feature sizes of 58 µm could be obtained using a nominal drop volume of 10 pl with printing resolution of 100 x 100 dpi and printing speed of 150 mm/s. Optical microscope images of Fig. 4 were taken after thermal curing on a hotplate (T_{hotplate}= 250 °C, t_{hotplate} = 30 min).

Figure 5 (a) shows well defined lines of OPSZ with sharp edges, inkjet-printed with resolution of 100 x 500 dpi and printing speed of 150 mm/s after annealing at 950 °C for 60 min. Figure 5 (b) illustrates a homogenous defect free area of OPSZ inkjet-printed with resolution of 500 x 500 dpi and printing speed of 150 mm/s. These optical microscope images confirm that no micro crack has been formed in the thin film even after annealing at 950 °C for 60 min.



(a) (b)

FIGURE 4. Jetted droplets of OPSZ in flight and on shiny etched surface of Si wafer (a) before optimization and (b) after optimization of printing parameters according to rheology of the ink.



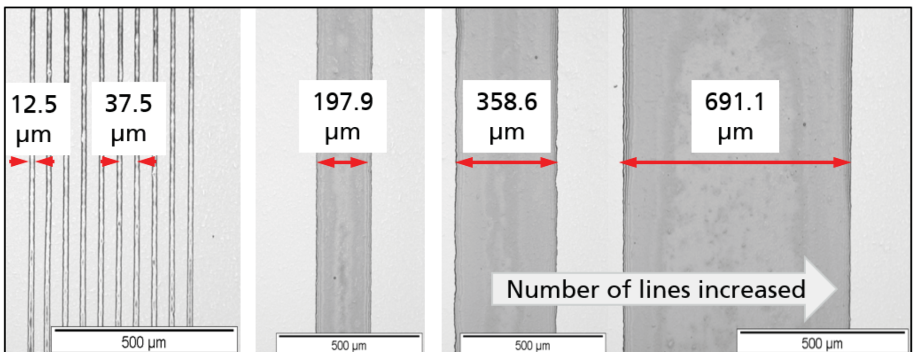
(a) (b)

FIGURE 5. Inkjet-printed (a) lines and (b) area of OPSZ ink on shiny etched surface of Si wafer after annealing at 950 °C for 60 min.

FlexTrail-printing

Polysilane

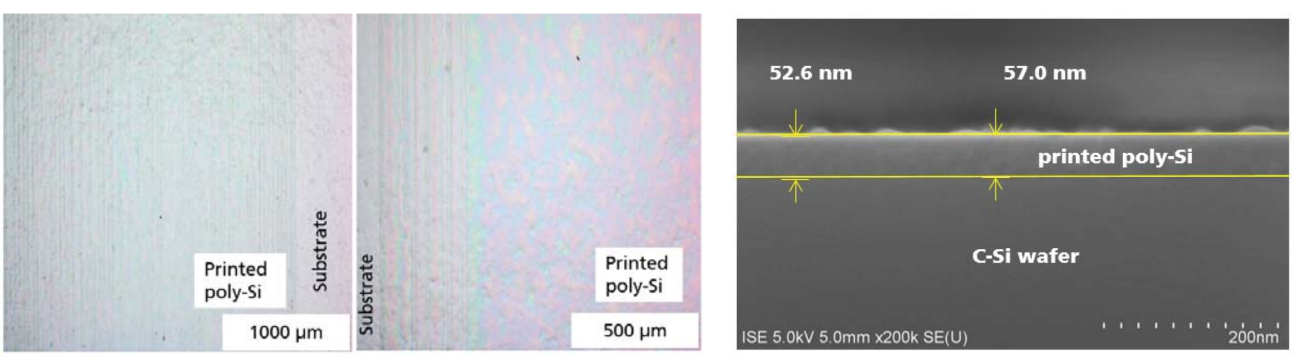
Figure 6 illustrates optical microscope image of FlexTrail-printed lines and areas of polysilane ink by means of adjusting printing speed and varying pitch (spacing between lines). These results obtained from simply printing UV polymerized CPS (light source: 3.5 watt, wavelength: 365 nm, distance from ink: 30 cm, exposure angle: 90 °, duration: 80 s) on shiny etched surface of Si wafer at 25 °C. A homogeneous coverage with the ink was achieved with pitch distances of 10 µm and printing speed of 50 mm/s on substrate at room temperature. From several experiments, we observed that interruption-free lines and closed thin films of polysilane can be obtained from FlexTrail-printing without requiring heating up the substrate. Furthermore, FlexTrail showed a high tolerance toward rheology of polysilane ink that changes with polymerization time (at a constant intensity) and volume percent of solvents in the ink). These observations imply great potential of the technology in printed Si field. As can be in Fig. 6, very narrow lines of polysilane can be printed with FlexTrail.



Printing speed (mm/s)	150	100	50	50
Pitch (µm)	50	10	10	10

FIGURE 6. Optical microscope image of FlexTrail-printed lines and areas polysilane ink on a shiny etched surface of Si wafer after its conversion into a-Si on a hotplate (T_{hotplate}= 400 °C, t_{hotplate} = 30 min).

FlexTrail-printed samples were annealed at 950 °C for 60 min to convert printed a-Si films into poly-Si and investigate formation of micro cracks. Optical microscope image of Fig. 7 (a) illustrates defect free and very homogeneous closed film of poly-Si obtained from FlexTrail-printing of polysilane ink. Scanning electron microscopy (SEM) cross sectional image of the sample confirmed that the poly-Si film is free of micro cracks with the thickness of ~55 nm that is in desired range for the target application.



(a) (b)

FIGURE 7. FlexTrail-printed poly-Si (a) Optical microscope image, (b) SEM cross section image.

OPSZ

Figure 8 illustrates optical microscope image of FlexTrail-printed well-defined line and homogeneous area of OPSZ after thermal curing on a hotplate ($T_{hotplate}$= 250 °C, $t_{hotplate}$ = 30 min). The result was achieved using pitch distances of 10 µm and printing speed of 50 mm/s on substrate at room temperature.

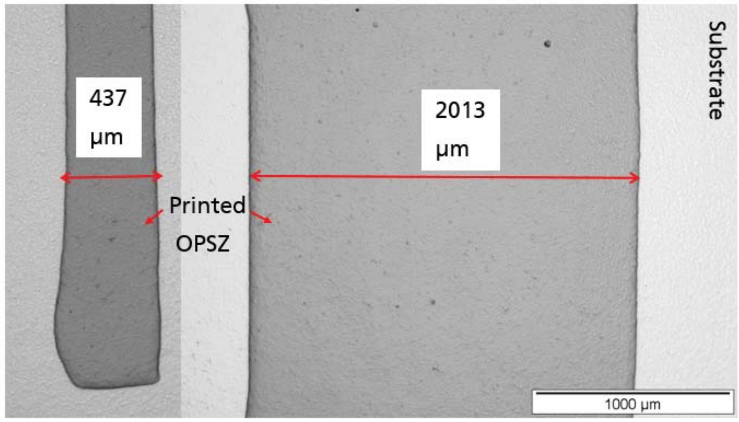


FIGURE 8. Optical microscope image of FlexTrail-printed OPSZ after thermal curing on a hotplate ($T_{hotplate}$= 250 °C, $t_{hotplate}$ = 30 min).

CONCLUSION

Reliable inkjet- and FlexTrail-printing processes were developed for polysilane and OPSZ inks. High frequency rheological properties of OPSZ were characterized and inkjet-printing processes and printhead temperature were tuned accordingly. Feature sizes of below 70 µm were obtained for polysilane and 60 µm for OPSZ by inkjet-printing. Homogenous, crack-free, closed thin-films of poly-Si/poly-SiC resulted from inkjet- and FlexTrail-printing of CPS and OPSZ inks after high temperature annealing. SEM analysis confirmed that thickness of printed films is in desired range for the target application (53 nm- 57 nm).

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REFERENCES

1. T. Masuda, Y. Matsuki, and T. Shimoda, "Stability of polydihydrosilane liquid films on solid substrates," *Thin Solid Films*, vol. 520, no. 15, pp. 5091–5096, 2012.
2. T. Masuda, M. Nakayama, K. Saito, H. Katayama, and A. Terakawa, "Inkjet Printing of Liquid Silicon," (eng), *Macromolecular rapid communications*, vol. 41, no. 23, e2000362, 2020.
3. T. Masuda, H. Takagishi, Z. Shen, K. Ohdaira, and T. Shimoda, "Phosphorus- and boron-doped hydrogenated amorphous silicon films prepared using vaporized liquid cyclopentasilane," *Thin Solid Films*, vol. 589, pp. 221–226, 2015.
4. T. Shimoda and T. Masuda, "Liquid silicon and its application in electronics," *Jpn. J. Appl. Phys.*, vol. 53, no. 2S, 02BA01, 2014.
5. T. Shimoda, Y. Matsuki, M. Furusawa, T. Aoki, I. Yudasaka, H. Tanaka, H. Iwasawa, D. Wang, M. Miyasaka, and Y. Takeuchi, "Solution-processed silicon films and transistors," (eng), *Nature*, vol. 440, no. 7085, pp. 783–786, 2006.
6. M. Trifunovic, P. M. Sberna, T. Shimoda, and R. Ishihara, "Solution-based polycrystalline silicon transistors produced on a paper substrate," *npj Flex Electron*, vol. 1, no. 1, 2017.

7. F. Kiefer, N. Wehmeier, M. Holthausen, C. Daeschlein, O. Wunnicke, C. Mader, and S. Kajari-Schröder, "Inkjet printing as a new method for the preparation of POLO contacts," *28th MRS Fall Meeting*, 2018.
8. J. Schube, T. Fellmeth, M. Jahn, R. Keding, and S. W. Glunz, "Inkjet- and FlexTrail-Printing with Low Silver Consumption for Silicon Heterojunction Solar Cells," *Phys. Status Solidi RRL*, vol. 13, no. 9, p. 1900186, 2019.
9. A. P. Cádiz Bedini, S. Muthmann, J. Allgaier, K. Bittkau, F. Finger, and R. Carius, "Liquid hydridosilane precursor prepared from cyclopentasilane via sonication at low temperatures without the action of light," (eng), *Ultrasonics sonochemistry*, vol. 34, pp. 289–293, 2017.
10. Z. Kiaee, C. Reichel, Z. Hussain, M. Nazarzadeh, J. D. Huyeng, F. Clement, M. Hermle, and R. Keding, "Inkjet printing of phosphorus dopant sources for doping poly-silicon in solar cells with passivating contacts," *Solar Energy Materials and Solar Cells*, vol. 222, p. 110926, 2021.