Inkjet Printed Top Contacts for Sustainable Solar Cells

Oliver M. Rigby[1], Bethany L. Willis[1], Prabeesh Punathil[1], Giray Kartopu[1], Matthew C. Naylor[1], Maarten van der Vleuten[2], Remi Aninat[2], Veronique Gevaerts[2], Vincent Barrioz[1], Guillaume Zoppi[1], Neil S. Beattie[1]

1. Department of Mathematics, Physics and Electrical Engineering, Northumbria University, Newcastle upon Tyne, NE1 8ST, U.K.
2. Solliance, TNO, Eindhoven, The Netherlands

Abstract — **An inkjet printer is used to deposit silver nanoparticle inks for use as top contacts on CIGS photovoltaic devices. Deposition and post-deposition treatments are optimized. The J-V characteristics of devices with inkjet printed Ag contacts are compared to devices with electron beam evaporated contacts with similar performance. Devices with copper contacts deposited by inkjet printing will also be presented. A life-cycle analysis study is also performed to determine the quantitative environmental impacts of using inkjet printing and it is found that the electricity usage is the greatest source, while replacing silver with copper is shown to have the next greatest contribution.**

I. INTRODUCTION

Silver is currently the most popular material for use as the top contact of solar cells as it is highly conductive, can be reliably deposited and does not react with the underlying layers. However, silver is expensive and global demand is expected to rapidly increase. For photovoltaics (PV), the predicted market growth necessary to meet global net zero commitments is expected to require approximately 85% of current silver reserves by 2050 [1]. As such, it is essential to minimize the quantity of silver used.

Depositing the top contacts of a solar cell on the research scale is typically performed using electron beam (e-beam) or thermal evaporation which requires vacuum conditions and wastes a significant portion of the silver target. Inkjet printing provides a novel alternative which requires significantly less energy (due to no vacuum being necessary) and is more efficient with material usage (due to less wasted material). As such, this work investigates the suitability of inkjet printing for PV applications. Activities include optimizing the deposition and post-deposition of silver inks to ensure robust and high performance patterns can be repeatably produced. Subsequently, silver contacts are deposited on complete PV devices with an absorber layer of $CuIn_xGa_{(1-x)}Se_2$ (CIGS). Alongside these activities a life-cycle analysis (LCA) is performed to quantitatively analyse the effects of inkjet printing.

II. METHODOLOGY

a). Inkjet Printing Details

A Fujifilm Dimatix-2850 Inkjet Printer was used to deposit Novacentrix JS-A211 Silver Nanoparticle inks (dispersed in glycol ether). In general, a droplet spacing of 20 µm was used and the piezoelectric heads had a voltage of 25 V.

b). CIGS Fabrication

On a 3 mm thick sodalime glass of 300 x 300 mm^2 deposition of the Mo back contact and Cu, In and Ga was done by pulsed DC sputtering inline. The Cu, In and Ga were subsequently transformed into CIGS in a selenisation oven at elevated temperatures. The resulting bandgap was targeted at 1.1 eV. CdS was deposited using chemical bath deposition, followed by RF sputtering of *i*-ZnO and ZnO:Al (AZO) [3].

c). Characterisation

Morphology of samples was investigated using a Tescan Mira 3 scanning electron microscope (SEM). Resistivity measurements were performed using Be-tipped contact probes with a Keithley 2400 sourcemeter. Current-voltage measurements of devices were carried out using a four-point contact probe, Keithley 2400 sourcemeter and an Abet Technologies Sun2000 11018 solar simulator.

d). LCA Methodology

LCA was performed using SimaPro V9.5.0.0 along with an Ecovinevent V3.9.1 database which provides the raw life cycle inventory data. For the LCA, the following functional unit is chosen: to provide a top electrical contact suitable for measuring the performance of 9 devices, each with cell area of 0.16 cm^2 and for one measurement per device. This provides a boundary on the quantity of material needed. A new cartridge and new ink must be used for each set of printing and so the material requirements for each of these are considered and proportioned accordingly with the functional unit. The material inventory of the printer is not included but the electricity usage is (as it is assumed that the lifetime of the printer is sufficiently great enough that the proportioned material costs are negligible for the functional unit). Similarly, the electricity usage of the hot plate for a subsequent heat treatment at 200ºC for 15 minutes is included but the material costs of the hot plate are not.

III. RESULTS AND ANALYSIS

To quantify the resistivity properties of the inks, they were deposited on indium-tin-oxide (ITO) coated glass. In order to determine resistivity properties (such as contact resistivity and

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Table 1. A summary of the effect of the different heat treatments on the deposited silver NP ink.

Heat Treatment	**Contact resistivity (Ωcm^2)**	**Bulk conductivity (as % of bulk Ag)**	**Grain size (nm)**
150ºC, 60 minutes	6	0.11	30
175ºC, 30 minutes	2 x10^{-1}	0.93	30
200ºC, 15 minutes	1.3 x10^{-2}	3.98	40 & 200

bulk resistivity), a continuous layer of material is needed and so multiple passes of the same pattern were performed to ensure sufficient material was present.

After deposition, the printed inks were subjected to a heat treatment with the purpose of removing any solvent and improving the conductivity by sintering the silver nanoparticles (NPs). Without any heat treatment, the deposited patterns were not conductive (due to glycol ether remaining). A range of heat treatments were considered and the following were found suitable: 150ºC for 60 minutes, 175ºC for 30 minutes and 200ºC for 15 minutes.

The post-deposition heat treatment has significant effects on the morphology and conductive properties of the deposited silver ink, as presented in Table 1.

The contact resistivity was determined using the Transfer Length Method (TLM). For this measurement (and bulk resistivity measurements), several lines were printed with dimensions of 10 mm by 0.3 mm. Noticeably the contact resistivity significantly decreases as the temperature of the heat treatment increases. Bulk resistivity measurements also showed a significant reduction in the resistivity (and hence increase in conductivity) of the samples as the temperature increased. Additionally, the grain size of the silver NPs was found to increase at higher temperatures (see Figure 1 inset). For the lower two heat treatments, only grains of size 30 nm were present but at 200ºC there were 40 nm size grains on top

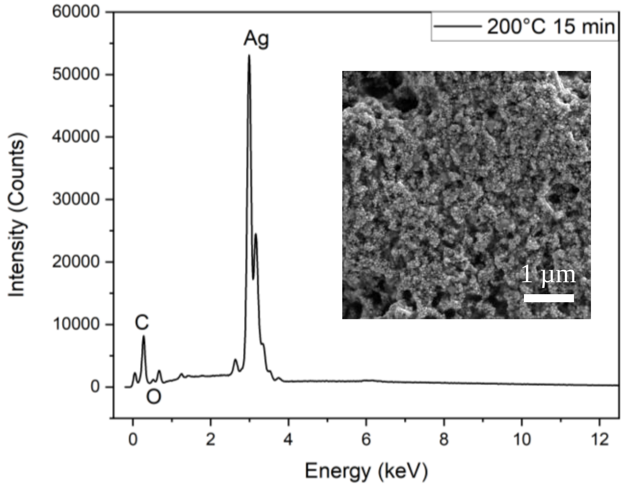


Fig 1. A map sum EDX spectrum of a 100 μm^2 area of the same sample with the Ag Lα line series at 2.98 keV, C (0.278keV) and O (0.51keV) peaks labelled. (Inset) SEM image of the silver NPs after a heat treatment of 200ºC for 15 minutes with 40 nm grains on top of 200 nm grains.

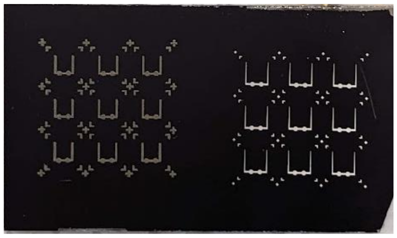
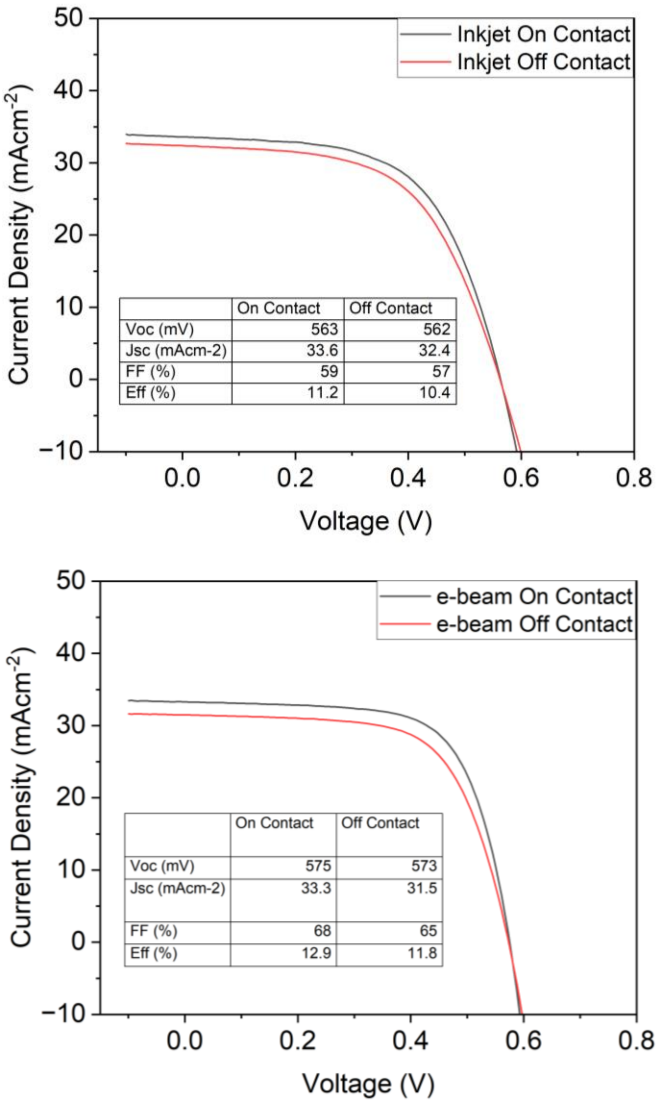


Fig 2. Nine cell masks of area 0.16cm^2 deposited using an inkjet printer (left) and e-beam evaporation (right). The whole sample has dimensions of ~2.5cm x 4.1 cm.



	On Contact	Off Contact
Voc (mV)	563	562
Jsc (mAcm-2)	33.6	32.4
FF (%)	59	57
Eff (%)	11.2	10.4

	On Contact	Off Contact
Voc (mV)	575	573
Jsc (mAcm-2)	33.3	31.5
FF (%)	68	65
Eff (%)	12.9	11.8

Fig 3. JV curves for a cell with inkjet printed contacts (top) and e-beam contacts, showing higher Jsc values for the measurement where the probes were on the contacts.

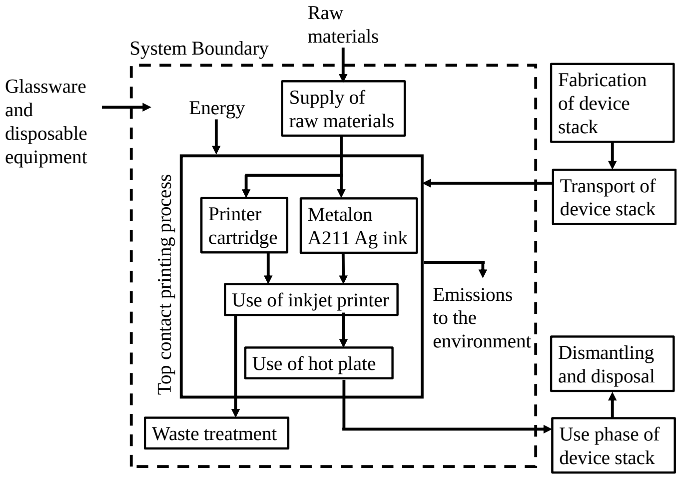


Fig 4. A system boundary diagram of the LCA of the inkjet printing process.

of 200 nm grains. This increase in grain size may explain the improved resistivity properties at 200ºC.

Additionally, energy-dispersive X-ray (EDX) analysis (see Figure 1) reveals that the samples heated to 200ºC were composed of a majority of Ag, with the dominant peaks owing to the Ag Lα line series. Minimal carbon is present suggesting the glycol ether has been removed and despite the heat treatments occurring in air, almost no O is present.

To test the performance of the inkjet printed silver inks as top contacts, they were deposited on devices made of a Mo/CIGS/CdS/i-ZnO/AZO stack and compared to silver contacts deposited by e-beam evaporation on the same sample (see Figure 2). Although the devices with inkjet printed contacts have a lower efficiency compared to devices with e-beam contacts, this is most likely due to variations of the device stack. Comparing performance results of the devices where the probes are on the silver contacts and on the AZO layer show improved device metrics (particularly J_{SC}) when using the silver contacts (see Figure 3). Measurements on the e-beam contacts show a relative efficiency increase of 10% compared to measurements off the contacts and similarly measurements on the inkjet printed contacts show a relative 7% efficiency increase. This shows that using inkjet printed silver for top contacts has comparable results to traditional e-beam deposition.

For the LCA, a system boundary diagram of the process is presented in Figure 4. Note that the post-deposition stage (in this case a hot plate) is considered essential to the printing process due to the otherwise poor resistivity values. The LCA results show that the greatest contribution comes from the electricity usage of the printer and the hot plate (~99.6% of total single score impact). In the future we look to replace the hot plate with photonic curing with the aim of reducing the electricity usage. Considering the parts which are not related to electricity usage, the largest contributors are the copper connections on each cartridge and the silver ink. Given that ~1/10 of a cartridge is required for a functional unit, this is not too surprising. When looking for ways to minimize the impact of the printing process it is therefore beneficial to consider a different ink as this is a factor which can be changed in the process. LCA results comparing copper ink to silver ink show a significant benefit to using Cu over Ag (see Figure 5). The largest improvement is to human health, due to the difference in the quantity of toxic chemicals used during refinement of the metals.

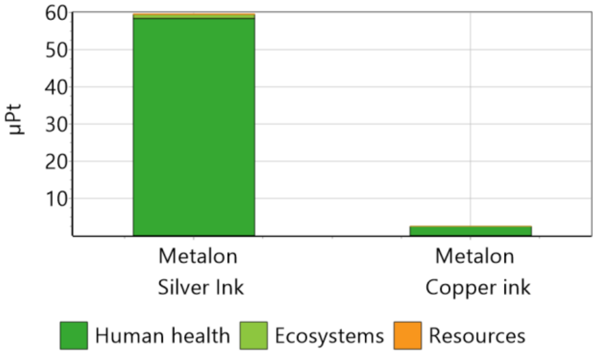


Fig 5. Single score LCA results comparing the use of silver ink to copper ink for equivalent masses of 2mg.

IV. SUMMARY AND FUTURE WORK

We have shown that using inkjet printed silver contacts gives comparable device performance to traditional contacts deposited using e-beam evaporation. A LCA of the process shows that electricity usage should be the primary focus for reducing impacts. Given this is difficult to control, we will also be printing Cu contacts and will present their effect on device performance.

REFERENCES

[1] B. Hallam, M. Kim, Y. Zhang, L. Wang, A. Lennon, P. Verlinden, P. Altermatt, P. Dias "The silver learning curve for photovoltaics and projected silver demand for net-zero emissions by 2050", *Prog. In PV: Res. And App.*, vol. 31(6) pp598-606, 2023

[2] Z. Wang, Z. Zhang, "Electron Beam Evaporation Deposition "*Advanced Nano Deposition Methods",* Wiley Online Library, 2016

[3] M.van der Vleuten, M. Theelen, R. Aninat, K. van der Werf, H. Mannetje, P. Reyes-Figueroa, T. Kodalle, R. Klenk, M. Simor, H. Linden "Control over the Gallium Depth Profile in 30x30cm^2 Sequentially Processed CIGS", *2020 47th IEEE Photovoltaic Specialists Conference (PVSC)*, pp 640-645, 2020