Novel Conductive Inks For 3D Printing

Preliminary Studies on Silver Ink Development and Curing Strategies

Ayala Kabla, Abd El Razek, Fernando de la Vega
PV Nano Cell Ltd.
Migdal Haemek, Israel
e-mail: ayala@pvnanocell.com, abd@pvnancell.com, fernando@pvnanocell.com

Leo Schranzhofer
Profactor GmbH
Steyr-Gleink, Austria
e-mail: leo.schranzhofer@profactor.at

***Abstract*— UV (ultraviolet) curable nanoparticle conductive inks for 3D printing present a novel solution for production of a wide variety of parts with integrated conductive circuits. Such inks are difficult to design due to the complex tradeoff between achieving high conductivity, obtainable by a high metal content ink, and requiring low ink viscosity in order to meet jetting requirements. Adding to that is the complexity of managing the competing curing and sintering processes of the printed polymer and metal constituents. In the current work, UV curable nanoparticle conductive inks have been formulated and tested by different curing and sintering techniques. It has been demonstrated that a low resistivity of less than 10 times the silver bulk resistivity is attainable by thermal sintering, even with non-conductive organic content of 60%. Photonic sintering demonstrated the ability to obtain a resistivity of below 60 times the silver bulk resistivity, which is higher than the resistivity obtained by thermal sintering, but achievable in shorter processing times within milliseconds.**

Keywords*— *printed electrtonics; 3D printing; silver ink; UV curable ink; curing; sintering; photonic sintering

I. INTRODUCTION

PV Nano Cell Ltd. provides a wide range of solvent based nano conductive Sicrys™ inks [1], available for printed electronics applications with 50 wt% (weight percent) solid concentration and six times bulk resistivity at 150 °C, 30 minutes thermal treatment. In order to expand its capabilities, PV Nano Cell is taking part in the EC (European commission) funded DIMAP project (Novel nanoparticle enhanced Digital Materials for 3D Printing and their application shown for the robotic and electronic industry), dealing with new materials for 3D printing [2]. PV Nano Cell will develop a novel UV curable nanoparticle conductive ink for 3D printing by PolyJet technology. The ink is based on PV Nano Cell's Sicrys™ silver nanoparticles, dispersed in a monomeric matrix from Stratasys Ltd. or GEO® specialty chemicals, formulated for reaching high conductivity of the cured/sintered tracks.

UV-curable inks have attracted increasing attention due to environmental considerations, fast curing speed, low energy consumption, fast overall manufacturing process, and the possibility to work with thermal sensitive substrates [3]. Moreover, UV irradiation has been demonstrated to be a viable alternative to thermal sintering. Polzinger et al. have shown resistivity values of about four times bulk silver after 80 seconds UV-sintering of commercially available Ag ink [4]. Hu Yating et al. have demonstrated the sintering of copper ink by UV irradiation for a few seconds, achieving a resistivity of 4×10^{-5} Ω·cm for antenna applications [5]. The ability of UV-irradiation to sinter Ag nanoparticles has opened up new paths to incorporate conductive features into the polymeric media. This makes UV-curable conductive inks attractive as they will benefit from both, fast curing and fast sintering.

In the market, however, mainly pastes with high viscosity and only a limited number of UV conductive inks are available. Among these, Polychem UV/EB International Corp. [6] and Tanaka Kikinzoku International (Europe) GmbH [7] pastes can be found, as well as a UV Ag flexographic ink from Gwent Group Ltd. [8]. The published resistivity values of these pastes and inks are 70-100 μΩ·cm.

The preparation of UV-curable conductive inks has been demonstrated in the literature. Sangermano et al. prepared UV-curable acrylic inks for printing resistors by incorporating Ag nanoparticles into a monomer; and reported a resistivity of $5x10^{3}$ $\Omega\cdot cm^{-1}$, which is an improvement of two orders of magnitude as compared to the pure polymeric matrix [3]. They also prepared UV-curable ink using Ag precursors; starting from silver hexafluoroantimonate and in-situ production of the Ag nanoparticles during the UV-irradiation [9], [10]. A hybrid Ag based ink prepared for an antenna printing application by Chiolerio et al. has shown 5% conductivity of bulk silver after thermal sintering at 250 °C for 30 minutes [11]. Zhai et al. shown conductivity of 7.14×10^{-5} Ω·cm for UV-curable ink after UV-curing and thermal sintering; they achieved the conductivity for the ink-jet printed ink after evaporation of water on a heating stage, curing under UV spot light source and sintering in a muffle furnace. Thus, they showed that even after curing, thermal treatment might lead to sintering of nanoparticles within the polymeric media [12]. Designing UV-curable conductive inks is challenging due to the complex tradeoff between good conductivity, achievable with high metal content, while maintaining both a low viscosity ink that meets jetting requirements and realizing fast curing rates. All the while, the ink constituents of metal nanoparticles and polymeric media must remain stable in the formulation.

 ISBN: 978-1-61208-496-1

TABLE I: FORMULATION COMPOSITION

	Wt.%	Wt.% from solids	Density (g/ml)	Vol %	Vol % from solids
Ag	50	86.06	10.49	7.34	40.37
Dispersant	1.1	1.89	1.21	1.40	7.70
PI	2	3.44	1.2	2.57	14.12
Monomer	5	8.61	1.12	6.88	37.81
Solvent	41.9	0	0.789	81.81	0.00

The main challenges facing this project include the ability to obtain a high solid content ink in a monomer matrix with suitable viscosity for jetting, and reaching percolation of particles in the sintered and cured printed pattern that will allow low resistivity. In order to overcome these hurdles, the formulation is carefully adjusted with appropriate additives and solvents for jetability, the solid content is raised so that percolation can be reached in the dried and cured samples, and alternative curing/sintering technologies to standard oven thermal treatments are being researched for short processing times.

The aim of this work was to investigate the curing and sintering behavior of the monomeric silver inks and understand the effect of the different monomers on the resistivity in order to choose the most promising monomers for further formulation optimizations. In order to do so, several curing/sintering approaches were tested, including: thermal treatment in an oven, UV irradiation, photonic sintering and curing monitoring by FTIR (Fourier-transformed infrared) spectroscopy.

Photonic sintering is a technique that uses pulsed light of a Xenon flash lamp to sinter thin films of particles.[13]–[19] It is a fast sintering method with common processing time in the range of milliseconds that operates at room temperature. The delivered light energy is selectively absorbed by the target particles and transferred to heat that triggers coalescence. Due to the pulsed shape of the flash, the heat transfer and therefore the damage to the substrate is low.

TABLE II: FORMULATIONS PREPARED WITH PI

sample #	monomer	viscosity @ 25 °C (cP)
	GEO	
D006	GM1	5.6
D009	GM2	5.6
D010	GM3	5.3
D011	GM4	5.7
D012	GM5	5.8
	STRATASYS	
D013	SM1	5.4
D014	SM2	5.4
D015	SM3	5.9

Thus, heat sensitive materials like polymers, paper or textiles can be used as substrate materials for printed electronics. The structure of this paper is as followed: in section II the performed experiments are described, followed by the discussion of the results in section III. In conclusion, section IV summarizes the presented work and gives a brief outlook on future work.

II. EXPERIMENTAL

Several different UV curable monomers were received from GEO (GM1-5) and Stratasys (SM1-3) and used as received, Ag nano particles were synthesized and prepared by PV Nano Cell.

A. Sample preparation:

1) Formulation preparation:

Sicrys™ Ag particles were incorporated into monomers at a 50 wt% Ag concentration. A volatile co-solvent was used in order to lower the viscosity of the formulation and evaporate quickly out of the printed tracks, resulting in a high solid Ag content of ~85 wt% Ag in the dried printed pattern (40 vol%). Formulations D006 through D015 (see also Table II), consisting of Ag, dispersant, photoinitiator (PI), monomer, and solvent constituents, were prepared according to the formulation composition indicated in Table I. For curing rate characterization of the monomers, samples were prepared keeping the same component ratio but excluding Ag and dispersant.

2) Curing:

Formulations D006-D015 were printed with a dispenser and dried on a hot plate at 50 ºC. The samples were then cured/sintered by each of the following methods:

- UV LED
- UV-LED + Oven
- Oven
- Photonic sintering

UV curing was performed with a 395 nm LED (light emitting diode) lamp and 2 min exposure time, and thermal treatment was performed in a box oven at 200 ºC for 1hr.

3) Sintering:

Ink samples on glass were freshly prepared by draw down bar printing (40 µm) on glass substrates followed by sintering. Photonic sintering was performed using a Heraeus flash system [20], with an emission spectrum between 200 to 1000 nm. The lamp setting was fixed for all the different ink formulations.

B. Sample Characterization:

The ink formulations were characterized for viscosity with a viscometer (Brookfield), and for particle size distribution and sedimentation rates using a centrifugal measurement technique (Lumisizer). In addition, curing rate was monitored by FTIR-spectroscopy (Brucker Tensor 37). Electrical performance was obtained by a four-point probe measurement set-up for resistance, and cross-section measurements were obtained using a surface profiler (Dektak IIA).

 ISBN: 978-1-61208-496-1

TABLE III: PRELIMINARY OBTAINED RESISTIVITY OF INDIVIDUAL TECHNIQUES

Sample	Resistivity (μΩ·cm)			
	UV LED	*UV LED + Oven*	*Oven*	*Photonic Sintering*
D006	N.A.	13 - 28	13 - 20	N.A.
D009	17 - 7e9	20	21 - 43	112 – 231
D010	212 - 2e9	10 – 13	10 - 15	638
D011	1e9 - 3e9	16 - 30	16-26	258
D012	900	50 - 82	77-92	62-85
D013	80 - 4e7	17 - 23	23	9-78
D014	50 - 83	38 - 72	50	723-1300
D015	15 - 270	12 – 17	15-18	87

III. RESULTS AND DISCUSSION

A. *Ink viscosities:*

Table II lists the formulations (D006 – D015) and their measured viscosity. The formulations slightly differ from each other due different GEO monomer (GM) and Stratasys monomer (SM) types

B. *Oven and UV curing/sintering*

As seen in Table III, the resistivity values resulting from the UV LED curing step alone are very high and the variation range of results is quite broad. After UV curing, the measured resistance from four-point probe was in the range of MΩ, though some measurement points showed lower resistances. The oven treatment, however, (with and without the UV curing step), significantly reduced the resistivity, along with a reduced variation in results.

Figure 1 shows the resistivity of the printed patterns as a function of line thickness for formulations prepared from different monomers, where UV cured and thermal oven treated samples are shown as filled data points, and thermally treated samples without UV curing are shown as un-filled data points.

As seen in the graphs, as the thickness of the samples increased, the resistivity increased as well. Thereby, the variation range of resistivity results indicated in Table III may have been due to line thickness variations of the printed samples.

C. *Photonic Sintering*

In addition to thermal and UV treatment, freshly prepared samples were photonically sintered. Hypothetically, matrix curing and particle sintering can take place in a single step and in a short period of time. In that way, samples D009, D012, D013 and D014 became conductive (low conductivity was determined) within a single flash experiment, although D014 showing the highest resistivity of the flashed samples using the stated setting. Samples D010, D011 and D015 on the other hand became conductive after a second flash. For Sample D006 no conductivity could be established.

D. *Monitoring Curing via FTIR:*

To investigate polymerization progress of the matrix, samples were prepared as described in the previous chapter. These samples were treated with UV light using a self-made UV-LED array in one minute steps. After each single step the irradiation was stopped for recording an IR-spectrum and irradiation was continued afterwards. For example, Figure 2 shows the decrease of the transmission-band at 1640 cm^{-1} corresponding to an α,β–unsaturated ketone (functional part of the acrylic monomer) over time for SM3. As can be seen, after two minutes of irradiation, there is no significant change indicating curing of most of the monomer content.

IV. SUMMARY AND CONCLUSION

It has been demonstrated that UV-curable low viscosity inks are feasible. Even with 60% by volume of non-conductive organic material, a resistivity of 10 μΩ·cm (6.3 times bulk silver resitivity) was achieved. In this work the curing step (UV radiation) did not sinter the Ag nano particles. This may stem from there being two competitive processes: the curing (cross-linking of the monomer) and the sintering of the nanoparticles; the curing being much faster than the sintering process therefore resistivities are high. As seen from thermal and UV LED sintering/curing treatments, there appears to be a dependence of the line thickness on the resulting resistivity, where thin lines achieve lower resistivity values. In addition, the UV LED conditions of 395 nm did not provide resistivity reduction of the printed tracks, and the oven treatment was a necessary step for achieving conductivity.

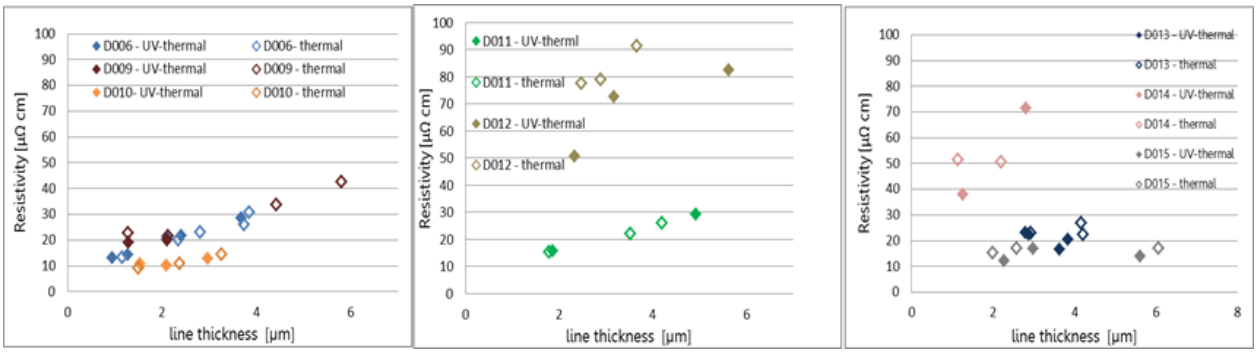

Figure 1: Resistivity of D006 – D015 formulations after UV-Thermal, and Thermal curing/sintering treatments.

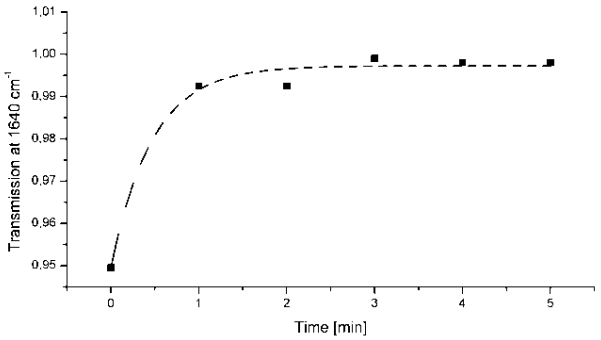

Figure 2. Curing progress based on FTIR spectroscopy. The data points correspond to the transmission recorded at 1640 cm^{-1}.

Another conclusion from the work is that the resistivity of the formulations differed from monomer to monomer. This might demonstrate the role of the monomer type on the percolation threshold or on the nano particle arrangement in the printed pattern. In addition, photonic sintering appeared to be a suitable method to cure and sinter the inks in one single step. Resistivity below 300 μΩ·cm was obtained after one and two flash experiments. Compared to the results for UV curing and thermal treatment, the measured resistances obtained from photonic sintering were higher. However, conductivity from flash sintering was achieved in a shorter period of time (within seconds).

Since the monomer matrix system was different in each of the ink formulations, the curing rates are expected to be different. The ideal setting for each ink has to be determined individually. The results shown here serve as a proof of concept for potentially using a photonic sintering strategy for monomeric inks. However, the flash parameters were not fully optimized in this preliminary experiment. Therefore, further work is necessary to find the optimal conditions for curing and sintering for each individual ink.

ACKNOWLEDGMENT

This project has received funding from the European Union's Horizon 2020 Programme for research and innovation under Grant Agreement No. 685937.

REFERENCES

[1] 'PVNanoCell - Home'. [Online]. Available: http://www.pvnanocell.com/. [Accessed: 17-May-2016].

[2] 'DIMAP: DIMAP'. [Online]. Available: http://www.dimap-project.eu/. [Accessed: 17-May-2016].

[3] M. Sangermano, A. Chiolerio, G. Marti, and P. Martino, 'UV-Cured Acrylic Conductive Inks for Microelectronic Devices', Macromol. Mater. Eng., vol. 298, no. 6, 2013, pp. 607–611.

[4] B. Polzinger, et al., 'UV-sintering of inkjet-printed conductive silver tracks', 2011, pp. 201–204.

[5] Y. Hu, B. An, C. Niu, W. Lv, and Y. Wu, 'Application of nano copper conductive ink for printed electronics', 2014, pp. 1565–1567.

[6] 'Welcome to Polychem UV/EB International Corp::Products (UV Curable Silver Conductive Inks)'. [Online]. Available: http://www.polychem.tw/index.php?module=product&mn=1&f=content&tid=30276. [Accessed: 17-May-2016].

[7] 'Tanaka Europe GmbH: Conductive Pastes'. [Online]. Available: http://www.tanaka-europe.eu/products/thin-thick-film-metallization/thick-film-pastes-precious-metal-powders/conductive-pastes/. [Accessed: 17-May-2016].

[8] 'The Gwent Group, Leaders in paste manufacturing, sensor/ biosensor development and Instrumentation .' [Online]. Available: http://www.gwent.org/gem_flexographics_pastes.html. [Accessed: 17-May-2016].

[9] A. Chiolerio, L. Vescovo, and M. Sangermano, 'Conductive UV-Cured Acrylic Inks for Resistor Fabrication: Models for their Electrical Properties', *Macromol. Chem. Phys.*, vol. 211, no. 18, 2010, pp. 2008–2016.

[10] A. Chiolerio, et al., 'Ag nanoparticle-based inkjet printed planar transmission lines for RF and microwave applications: Considerations on ink composition, nanoparticle size distribution and sintering time', *Microelectron. Eng.*, vol. 97, 2012, pp. 8–15.

[11] A. Chiolerio, V. Camarchia, R. Quaglia, M. Pirola, P. Pandolfi, and C. F. Pirri, 'Hybrid Ag-based inks for nanocomposite inkjet printed lines: RF properties', *J. Alloys Compd.*, vol. 615, 2014, pp. S501–S504.

[12] D. Zhai, T. Zhang, J. Guo, X. Fang, and J. Wei, 'Water-based ultraviolet curable conductive inkjet ink containing silver nano-colloids for flexible electronics', *Colloids Surf. Physicochem. Eng. Asp.*, vol. 424, 2013, pp. 1–9.

[13] J. West, J. Sears, M. Carter, and S. Smith, *Photonic sintering of silver nanoparticles: comparison of experiment and theory*. INTECH Open Access Publisher, 2012.

[14] R. Abbel, T. van Lammeren, R. Hendriks, J. Ploegmakers, E. J. Rubingh, E. R. Meinders, and W. A. Groen, 'Photonic flash sintering of silver nanoparticle inks: a fast and convenient method for the preparation of highly conductive structures on foil', *MRS Commun.*, vol. 2, no. 4, 2012, pp. 145–150.

[15] D. J. Lee, S. H. Park, S. Jang, H. S. Kim, J. H. Oh, and Y. W. Song, 'Pulsed light sintering characteristics of inkjet-printed nanosilver films on a polymer substrate', *J. Micromechanics Microengineering*, vol. 21, no. 12, 2011, p. 125023.

[16] J. Niittynen, E. Sowade, H. Kang, R. R. Baumann, and M. Mäntysalo, 'Comparison of laser and intense pulsed light sintering (IPL) for inkjet-printed copper nanoparticle layers', *Sci. Rep.*, vol. 5, 2015, p. 8832.

[17] H.-J. Hwang, K.-H. Oh, and H.-S. Kim, 'All-photonic drying and sintering process via flash white light combined with deep-UV and near-infrared irradiation for highly conductive copper nano-ink', *Sci. Rep.*, vol. 6, 2016, p. 19696.

[18] K. C. Yung, X. Gu, C. P. Lee, and H. S. Choy, 'Ink-jet printing and camera flash sintering of silver tracks on different substrates', *J. Mater. Process. Technol.*, vol. 210, no. 15, 2010, pp. 2268–2272.

 ISBN: 978-1-61208-496-1

[19] Nanotechnology Conference and Trade Show, M. Laudon, B. F. Romanowicz, and Nano Science and Technology Institute, Eds., *NSTI Nanotech 2006: 2006 NSTI Nanotechnology Conference and Trade Show, Boston, May 7-11, 2006*. Boston [Mass.]: Nano Science and Technology Institute, 2006.

[20] 'Heraeus Flash Lamp System'. [Online]. Available: https://www.heraeus.com/en/hng/products_and_solutions/arc_and_flash_lamps/flash_lamp_systems.aspx. [Accessed: 17-May-2016].

 ISBN: 978-1-61208-496-1