

Screen-Printing of Conductive Nanomaterial Inks for Stretchable Electronics

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Abstract—Screen-printing process has been known for decades as an integral part of thick-film technology. Lately, it has been recognized as a possible means of pattern formation for stretchable electronic devices commonly used in fitness monitoring, epidermal and wearable healthcare. These devices are formed on thin stretchable substrates in combination with nanocomposites based on polymeric binders and conductive fillers. The objective of this paper is to present challenges that screen-printing process for stretchable electronics is facing such as key process requirements and parameters, selection of stretchable substrates, properties of conductive nanomaterial inks and strain management near rigid areas.

Keywords—screen-printing process; stretchable electronics; conductive nanomaterials; polymeric substrates; rigid areas; strain concentration area

I. INTRODUCTION

When microelectronic technologies are in question, screen-printing process is usually related to thick-film technology where it has been used for realization of custom electronic devices, heating elements, integrated passive devices and, in recent years, sensors and thick-film micro-electro-mechanical (MEMS) structures on ceramic and silicon substrates [1-3]. It is a mature and relatively simple process that does not require major investments. However, it offers high pattern resolutions on versatile substrates. For these reasons, screen printing process is being recognized as a possible means of pattern formation on stretchable electronic devices commonly used in epidermal and wearable healthcare (blood pressure monitoring and electrocardiography) as well as in fitness monitoring.

Stretchable electronic devices are designed to operate under high levels of deformation while maintaining full electrical integrity. They are formed on thin stretchable substrates, usually thermoplastic polyurethanes and polydimethylsiloxanes in combination with conductive inks [4]. Conductive inks are nanocomposites based on polymeric binders and conductive fillers. Filler particles that are immersed in polymer matrix form rigid inclusions and their contacts govern the conduction, while polymer matrix carries deformation transferred from the strained substrate.

Stretchable electronic devices often include surface-mounted devices (SMDs). SMDs, such as rigid passive components, integrated circuits, batteries, connectors, etc., form rigid islands [5] that tend to affect electromechanical behavior of the device. Strain concentration in the vicinity of these rigid areas usually leads to fracture of conductive paths and consequentially to device failure.

Reliability of screen-printed conducting lines depends on a number of parameters such as substrate and composition used, screen-printing parameters, rigid-to-soft connections, etc. Because of its importance, this paper will address some of the key issues of the screen-printing process for stretchable electronics.

II. SCREEN-PRINTING PROCESS FOR STRETCHABLE ELECTRONICS

Screen-printing is a well-known contact printing method. During the screen-printing process, squeegee passes conductive ink through the screen mash transferring it to a selected substrate. While the contact between screen and the substrate lasts, conductive ink adheres both to screen mash and substrate. As the mash is being pulled away from the substrate, the ink forms filament structures until the cohesive forces are overpowered, leading to a pattern formation on the substrate (Fig. 1.).

According to [6] the screen-printing process can be divided into following stages:

- A Ink adheres to the substrate
- B As the mash is being pulled away from the substrate the ink structure extends.
- C Ink flows into filament structure.
- D Two ink structures (adhered to the substrate and to the mash) are being separated.

Impact of the squeegee reduces viscosity of the ink allowing easier ink flow through the mash. Fine mash screens provide desired resolutions of printed conductive lines. Printed conductive line thicknesses are determined by screen emulsion,

material that allows formation of desired patterns using UV imaging. Mash count and emulsion thickness determine imaging times and, consequentially, line definition. Fine meshes in combination with thick emulsions require longer imaging times and, as a result, conductive line definition deteriorates. Wear of the screen depends of the operating times, squeegee durometer, applied pressure and snap-off distances.

It should be noted that conductive lines screen-printed on flexible substrates for applications in stretchable electronics require far better resolutions than lines for conventional thick-film technology applications. Unlike flexible polymer substrates, ceramic substrates and silicon wafers are not always smooth and texture variations (up to 10 μm [3]) may result in poor edge definitions due to bleeding. Since bleeding strongly depends on the paste rheology and substrate roughness, thin layers of screen-printed inks for stretchable electronics are not affected by this effect.

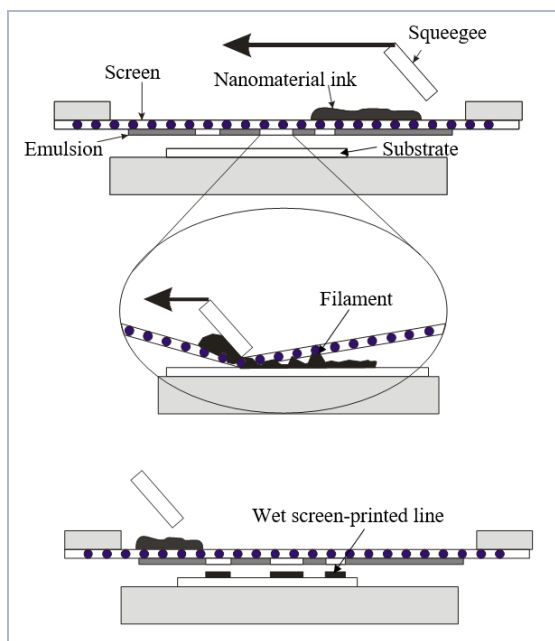


Figure 1. Screen-printing process

When screen-printed stretchable electronics is in question basic requirements include:

1. printability of the conductive ink (fine line printing)
2. compatibility with the stretchable substrate,
3. high conductivity of the ink and
4. ability to withstand repeated operation under strain.

As substrates for screen-printed stretchable electronics thermoplastic polyurethanes (TPUs) and polydimethylsiloxanes (PDMS) are usually used. TPU is often used because of its thermoformability and high abrasion resistance. Since it has high surface energy, it provides better adhesion between conductive ink and substrate than PDMS without any additional surface treatment [4]. Flexible substrates are usually about 50 μm thick [4] and able to withstand high levels of deformation without substrate failure. Prior to printing, soft

substrate must be attached to a metal plate in order to secure a flat surface for the screen-printing process.

For screen-printing process semiautomatic screen printers are usually used in combination with screens realized using aluminum frames and polyester meshes. Conductive nanomaterial inks often require multiple printing cycles in order to achieve desired conductive path thicknesses. After the screen-printing process, printed ink is annealed in an oven at the designated temperature compatible with polymer substrate, usually 120-125 $^{\circ}\text{C}$, depending on the type of polymer matrix [4]. The curing temperature of the conductive ink must be lower than the softening temperature of the flexible substrate (for example, softening temperature for TPU is 155–185 $^{\circ}\text{C}$).

III. CONDUCTIVE NANOMATERIAL INKS

Stretchable electronics are based on highly conductive nanomaterial inks that have to withstand strains of at least 20 % [4, 7] as needed for epidermal and wearable healthcare applications (Fig. 2). Conductive nanomaterial inks consist of conductive filler immersed in stretchable polymer matrix, usually polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA)/polyvinyl pyrrolidone (PVP) blend or polydimethylsiloxane (PDMA) [7-9].

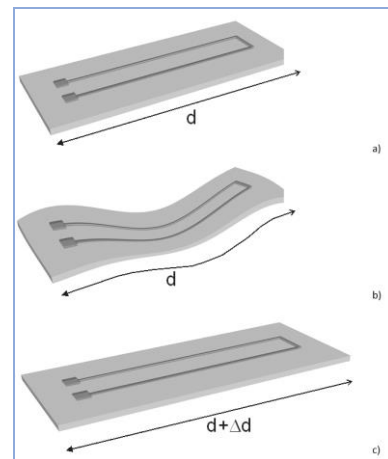


Figure 2. Rigid (a), flexible (b) and stretchable (c) conductive lines

Ink performances are mainly governed by rheological and geometrical properties of the conductive filler. Conductive filler has the tendency to agglomerate due to strong intermolecular forces, especially when spherical nanoparticles are in question. Agglomeration results in reduced dispersion of the filler throughout the matrix. Large conductive particles are not suitable for fine line printing and may lead to line fracturing. Percolation thresholds that are defined as the minimum volume fractions of conductive fillers required to construct continuous electrical pathways in a given composite material, are related to conductive material loading [10]. Heavy loading limits both printability and stretchability of the conductive ink.

Conductivity of these conductive nanomaterial-polymer composites can be analyzed and predicted using the percolation theory that describes connectivity between randomly distributed conducting particles in an insulating medium [11-12]. Low conductive filler contents sufficient to form

percolation networks are desirable because they minimize deterioration of the polymer matrix properties. Also, they are being used in applications where transparency is required.

Stretchable electronics often use silver-based nanomaterial conductive inks. Spherical silver nanoparticles and silver nanowires are being used as conductive fillers [13-14]. Spherical Ag nanoparticles tend to form agglomerates due to strong interparticle forces. High percolation threshold also affects inks properties. For these reasons dispersion is limited and high material loading is required.

Silver nanowire inks, because of Ag nanowire elongated geometry, tend to form conductive networks at low conductive material loadings (Fig. 3). However, further improvements related to dispersion, rheology, and sintering should be made.

Carbon nanotubes (CNT) have excellent elastic and electrical properties. However, their dispersion is strongly affected by powerful interparticle forces and CNT based inks have to overcome technical challenges regarding choice of optimum combination of solvents and additives that would provide adequate ink rheology.

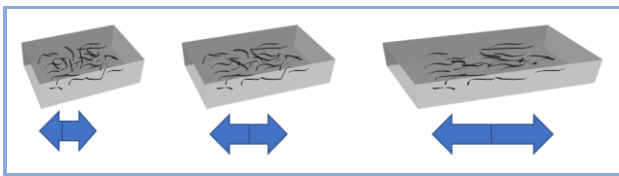


Figure 3. AgNW-based conductive nanomaterial ink: Ag nanowire elongated geometry, tend to form conductive networks at low conductive material loadings

Interconnects realized using these materials measured resolutions down to $50\ \mu\text{m}$ [7, 14] and sheet resistances of approximately $35\text{-}50\ \text{m}\Omega/\text{sq}$ [4, 14], a value sufficient for most electronics applications.

IV. RIGID AREAS

Simple stretchable electronic devices usually comprise stretchable substrate, screen-printed conductive ink and rigid components that affect electromechanical properties of the system. Commonly used rigid components are batteries, connectors, passive components, integrated circuits, etc. In order to reduce strain concentration, especially when complex devices are in question, arrangement of the components must be optimized. To limit the straining effect in the vicinity of rigid islands shielding frames are usually introduced [5]. These shielding frames are introduced in order to reduce strain concentrations near vulnerable regions of the substrate. However, they sometimes cause secondary effects that lead to delamination of stretchable conducting paths. In [5], three types of fundamental approaches to strain reduction were presented (Fig. 4):

1. local rigid component encapsulation,
2. direct rigid component shielding and
3. strain dispersion.

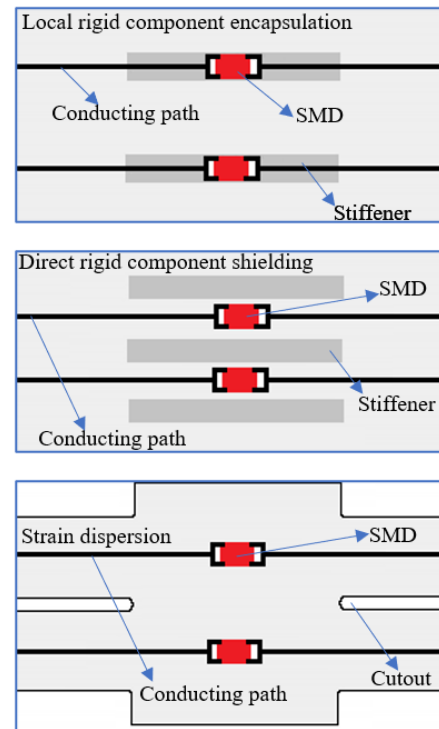


Figure 4. Strain concentration reduction [5]

When local rigid component encapsulation is in question, strips of polymer material compatible with the substrate are being added locally using hot press binding process, in the vicinity and under the SMD in order to increase substrate stiffness locally, around the component. This type of strain reduction induces additional straining in other critical parts of the system that may lead to conducting path cracking.

Direct rigid component shielding introduces strips of polymer material on both sides of each rigid component to relieve strain from printed conducting paths. Similar to local rigid component encapsulation, this type of shielding relieves stress in the vicinity of the rigid component, but causes additional straining in areas of stiffened to soft area transition that increases straining of stretchable conducting paths.

Strain dispersion is based on substrate material removal in order to create lower stiffness areas and disperse strain more evenly throughout the device. This process does not involve placement of additional material and may be introduced as a regular part of the realization process, as the part of the substrate cutting stage.

Local and direct rigid component shielding strategies both use strips of polymer material in vicinity of the rigid component. Although the strain is being partially relieved around rigid component, conduction paths still experience significant straining that may lead to failure. Number and size of rigid components govern the choice of the strain managing strategy. Strain dispersion, being an integral part of the production process, is the easiest way to reduce strain concentrations near vulnerable regions of the stretchable substrate.

For SMD and connector attachment on the top of the interconnecting pads, flexible conductive adhesives are used and cured at designated temperatures that are sufficiently low

not to interfere with integrity and properties of both the substrate and printed structure.

V. CONCLUSION

Stretchable electronics integrate a wide variety of soft materials that, unlike rigid systems, interface well with human body. The key feature of these systems are highly conductive electrical interconnections that maintain their structural integrity with strain. Screen-printing process as a mature contact printing method offers high control over pattern deposition, print resolution, and substrate choice.

Several essential requirements must be met to fabricate stretchable electronics via screen-printing. Conductive nanomaterial ink must be compatible with the stretchable substrate (TPU, PDMS, etc.) and able to provide adequate printability and line resolution. In order to withstand strains of at least 20 %, highly conductive nanomaterial inks must have proper rheology. Conductive nanomaterial filler (silver nanoparticles and nanowires, carbon nanotubes), solvent, binder, and rheological agent solutions must be selected in accordance with fluid dynamics of the screen-printing process.

There are two materials of choice for screen-printed stretchable electronics: Ag nanowires and carbon nanotubes. Ag nanowires due to their elongated geometry allow conductive network formation at low material loadings, but further investigations related to dispersion, rheology, and sintering are necessary. Carbon nanotubes have excellent elastic and electrical properties but ink rheology requires further improvements.

Rigid components such as batteries, connectors, passive components, integrated circuits, etc. induce strain concentrations that affect electromechanical properties of the system. Among three types of fundamental approaches to strain concentration reduction (local rigid component encapsulation, direct rigid component shielding and strain dispersion), strain dispersion is the most convenient one. Being an integral part of the production process, strain dispersion is the easiest way to reduce strain concentrations, although position and number of rigid parts may require application of strips of polymer material near/at critical parts of the system.

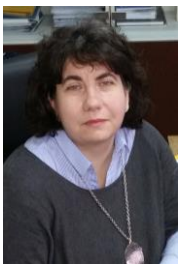
In general, screen-printing is a promising method for stretchable electronics realization. However, commercial use requires further investigations related to ink rheology, conductive filler dispersion, percolation network formation, strain concentration management etc.

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REFERENCES

- [1] O. Aleksić, M.V. Nikolić, M. Luković, Z. Stanimirović, I. Stanimirović, L. Sibinoski, "The Response of a Heat Loss Flowmeter in a Water Pipe Under Changing Flow Conditions", *IEEE Sensors Journal*, Vol. 16, No. 9, pp. 2935 - 2941, May 2016.
- [2] Z. Stanimirović, I. Stanimirović, "Pt Resistive Film Sensors", *Proceedings of 31st International Conference on Microelectronics - MIEL 2019*, pp. 145-148, Niš, Serbia, September 16th-18th, 2019.
- [3] I. Stanimirović, Z. Stanimirović, "Screen printing process for solar cells", 9th International Conference on Renewable Electrical Power Sources ICREPS 2021 Belgrade, Serbia, October 2021.
- [4] J. Suikkola, T. Björnin, M. Mosallaei, T. Kankkunen, P. Iso-Ketola, L. Ukkonen, J. Vanhala, M. Mäntysalo, "Screen-Printing Fabrication and Characterization of Stretchable Electronics", *Scientific Reports*, 6(1):25784, May 2016.
- [5] D. Di Vito, M. Mosallaei, B. Khorramdel, M. Kanerva, Mikko & M. Mäntysalo, "Mechanically driven strategies to improve electromechanical behaviour of printed stretchable electronic systems", *Scientific Reports*, 10(1), July 2020.
- [6] N. Kapur, S. J. Abbott, E. D. Dolden and P. H. Gaskell, "Predicting the Behavior of Screen Printing," *IEEE Transactions on Components, Packaging and Manufacturing Technology*, Vol. 3, No. 3, pp. 508-515, March 2013.
- [7] Q. Huang, Y. Zhu, "Printing Conductive Nanomaterials for Flexible and Stretchable Electronics: A Review of Materials, Processes, and Applications", *Advanced Materials Technologies*, Vol. 4, Issue 5, May 2019.
- [8] S. Choudhary, R.J. Sengwa, „ZnO nanoparticles dispersed PVA–PVP blend matrix based high performance flexible nanodielectrics for multifunctional microelectronic devices", *Current Applied Physics*, 18(9), pp. 1041-1058, 2018.
- [9] P. Feng, M. Zhong, W. Zhao, "Stretchable multifunctional dielectric nanocomposites based on polydimethylsiloxane mixed with metal nanoparticles", *Materials Research Express*, Vol. 7, No. 1, 2020.
- [10] Choi, S. Han, D. Kim, T. Hyeon, D.H. Kim, „High-performance stretchable conductive nanocomposites: Materials, processes, and device applications", *Chemical Society Reviews*, 48, pp. 1566-1595, 2019.
- [11] M.M. Jevtić, Z. Stanimirović, I. Mrak, "Low-Frequency Noise in Thick-Film Resistors due to Two-Step Tunneling Process in Insulator Layer of Elemental MIM Cell", *IEEE Transactions on Components, Packaging, and Manufacturing Technology-Part A*, Vol. 22, No. 01, pp. 120-125, March, 1999.
- [12] I. Mrak, M.M. Jevtić, Z. Stanimirović, "Low-frequency Noise in Thick-film Structures Caused by Traps in Glass Barriers", *Microelectronics Reliability*, 38, pp. 1569-1576, 1998.
- [13] L. Zhang, T. Song, L. Shi, N. Wen, Z. Wu and C. Sun, "Recent progress for silver nanowires conducting film for flexible electronics", *Journal of Nanostructure in Chemistry*, Vol. 11, Issue 3, Sept. 2021.
- [14] N. Zavanelli, W.-H. Yeo, "Advances in Screen Printing of Conductive Nanomaterials for Stretchable Electronics", *ACS Omega*, 6, pp. 9344-9351, 2021.



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