International Journal of Nanoelectronics and Materials
Volume 13 (Special Issue) May 2020 [431-438]

The Effect of Temperature on the Electrical Conductivity and Microstructure Behaviour of Silver Particles

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ABSTRACT

Silver conductive ink has been used in the electronics industry due to their potential advantages such as high electrical conductivity and thermal conductivity. However, silver needs to undergo a curing process to reduce the porosity between particles as well as to have a smooth conductive track to ensure maximum conductivity. Therefore, the effect of temperature on the electrical conductivity and microstructure were explored. The printing of silver conductive paste was executed on a polymer substrate through screen printing before analysis. Next, an electrical analysis was done to measure the conductivity by using a 4-point probes instrument, followed with microstructure and mechanical analysis which were carried out to observe the structure behaviour and hardness of silver respectively with respect to temperature. The study found that the electrical conductivity of silver increases when temperature elevated. Besides that, the microstructure of silver has a larger size with the increase in temperature, correspondingly cause the silver to have less hardness. In conclusion, temperature plays significant roles in increasing the electrical conductivity of silver.

Keywords: Silver Conductive Ink, Temperature, Conductivity.

1. INTRODUCTION

Conductive ink can be inorganic material and organic material [1]. The inorganic material is where the metallic nanoparticles such as copper, silver, and gold dispersed in the matrix solution and commonly used for the production of passive components and transistor electrodes [1]. While organic material or ink comprises of organic material such as a polymer that can be classified into three types which are conductor, semiconductor and dielectric. High conductive-based polymer ink is commonly employed in batteries, capacitors, and resistor while semiconductor-based polymer ink act as active layers such as in Organic Light-Emitting Diodes (OLEDs), sensor, and many more [1]. Before choosing suitable conductive ink to use, there are requirements need to consider according to on their attributes such as electrical conductivity, suitability for printing substrate, work function, oxidation stability, fabrication technique, and cost. The conductive inks must exhibit excellent electrically conductive performance by incorporating conductive filler (silver, copper and gold). Silver nanoparticles have been the most promising conductive ink and an alternative to the current ink used in the printed technology industry which is copper [2-5]. In the printing technology, usage of silver as ink give advantages as it can bond and cure at a low-temperature range of 473-573K [6-10]. The study by Gao *et al.* [11] reported silver as a conductive filler that has the highest electrical and thermal conductivity

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(6.3 x 107 Sm-1 and 429W m-1 K-1 respectively) compared to other materials such as copper. In addition, the silver paste was claimed to perform better physical and electrical performance, hence makes the silver favoured among researcher [12-14]. Reviewed by Tobjörk and Österbacka [12] on conductive material also explained that silver has the lowest bulk resistivity (1.59 μΩ cm) among all metals [12].

Although conductive ink consists of a high amount of silver particles benefited in term of electrical performance, however, the post-printing process which is curing with higher temperature need to be performed to have a continuous conductive solid track. Besides, this step helps in eliminate the stabilizer and solvent from conductive ink. Elimination of this ingredient is essential as they will create a problem in term of the electrical performance of the ink [15].

2. MATERIAL AND METHODS

2.1 Test Sample and Pattern

Thermoplastic Polyurethane (TPU) was supplied from Takeda Sangyo, and used it as received. Material has a thickness of 100 μm with an optically transparent polyester film. Screen printing was executed to print conductive silver ink pattern on the TPU with a dimension of 7 cm length × 7 cm width. The substrate was first cleaned with ethanol to eliminate any contamination on the surface before printing was conducted. The commercial conductive silver paste was used in this study. The post-treatment step was conducted by curing in the oven at various temperatures: (1) room temperature, (2) 60°C, (3) 80°C, (4) 100°C, (5) 120°C, (6) 130°C, and (7) 140°C. The prepared test pattern of silver is presented in Figure 1.

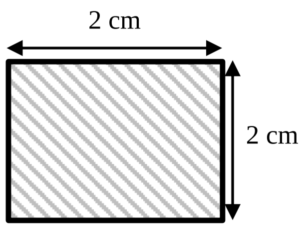

Figure 1. The test pattern of printed silver on TPU substrate.

2.2 Resistivity Measurements

The electrical resistivity of silver after curing at different temperatures was measured to investigate the effect of temperature on the conductivity of silver. Measurements were done using four-point probe measurement (Jandel RM3000). The current supplied was fixed to 100mA, and sheet resistance was measured at 6 different points to ensure reliable reading. The sheet resistance was measured according to Equation (1).

$$R_{square} = cf \times \frac{V}{I} \tag{1}$$

where *cf* is a correction factor that was assumed to be 4.53, *V* is the voltage between the inner probe, and *I* is the current supplied.

2.3 Microstructure Analysis

Scanning Electron Microscopy (SEM) was used to observe the microstructure behaviour of the silver paste with respect to temperature. The micrograph of SEM was acquired with JEOL JSM-6010PLUS/LV at an accelerated voltage of 10 kV. Energy Dispersive X-Ray Analysis (EDX) was carried out on silver paste at room temperature. EDX spectrum of silver paste indicates a silver content of 21.43 atom % followed by O (16.04 atom %) and Cl (4.34 atom %).

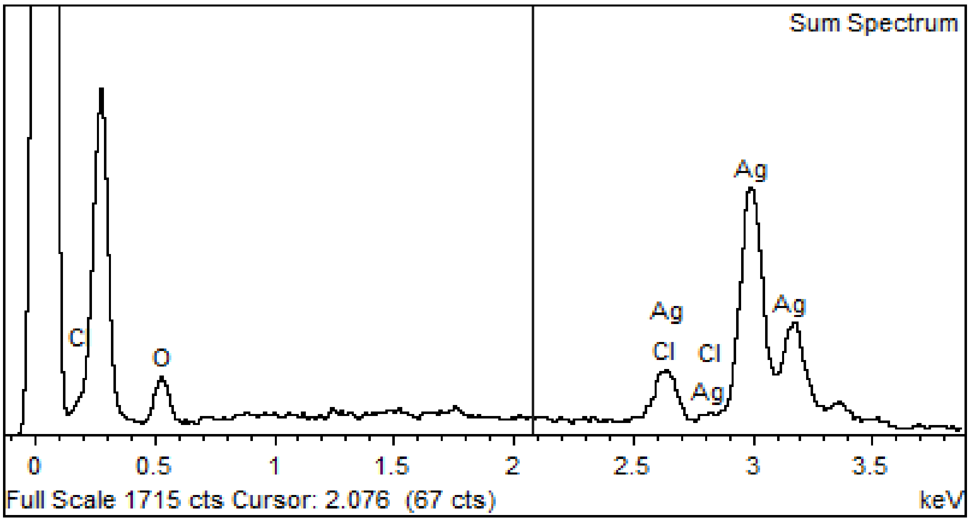

Figure 2. EDX spectrum of silver conductive ink.

2.4 Nanoindentation Analysis

Nanoindentation was conducted to analyse the mechanical properties of printed ink on the substrate at the nanoscale. Measurement was performed by nanoindenter (DUH-211S Dynamic Ultra Micro Hardness Tester) on the specimen. The nanoindenter operation involves loading a small diamond tip into the sample while measuring its displacement into the surface to climb up or down in order to reach the saturation value.

3. RESULTS AND DISCUSSION

Figure 3 shows that the sheet resistance decreases as temperature increases. The plotted graph showed the resistance decreases from approximately 153 mΩ/ϒ to 21 mΩ/ϒ when temperature elevated from room temperature to 140°C, respectively. The sheet resistance showed a sharp decline from room temperature to 60°C, indicating the densification of silver particles initiated. As temperature continuously elevated, the resistance keeps decreasing gradually until it reaches a value of approximately 21 mΩ/ϒ or 0.021 Ω/ϒ at the highest temperature of 140°C. At this temperature, the resistance is approximately around the value of silver in the previous study ranging between 0.01-0.04 Ω/ϒ [16]. The study of the correlation of resistance with temperature had been proven by many researchers that high temperature allowed the reduction of resistance [17–19].

When temperature keeps elevated, the diffusion between silver will initiate. The silver will undergo nucleation, and the size of the silver particles start to become larger as particle diffuse with particle contact with each other when temperature elevates, as illustrated in Figure 4. When the temperature increased, the gap between each particle reduced, hence diffusion can take place. The diffusion of particles causes the appearance of the necking structure. The necking structure becomes broader and thicker as the temperature continuously increases. In addition, the diffusion of particles causes a reduction in the grain boundary of particles, hence resulting in the silver with less hardness. Therefore, the silver nanoparticles are found to be well interconnected to form a smooth structure at a higher temperature.

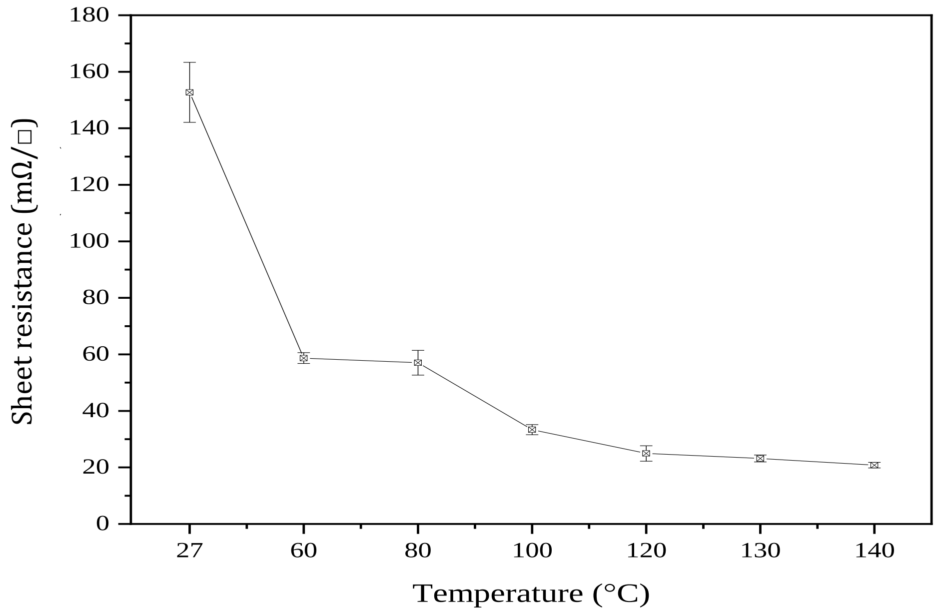

Figure 3. Effect of temperature on the conductivity of silver.

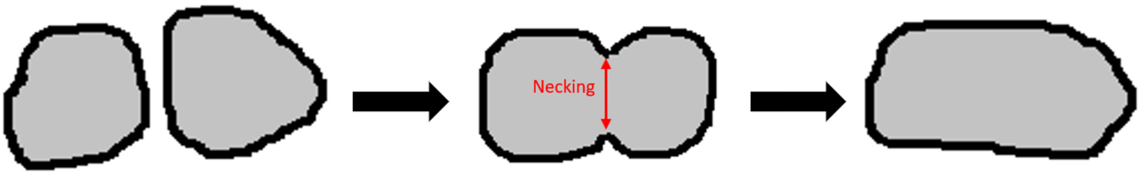

Figure 4. The grain diffusion initiates when temperature elevated

To have a better insight into this event, investigation of silver grain microstructure with respect to temperature was observed. Figure 5 displayed SEM micrograph of silver particles at different temperatures: room temperature, 60°C, 80°C, 100°C, 120°C, 130°C and 140°C. In the figure, a high distribution of small particles was seen at room temperature, and the number of particle distribution start to decrease as temperature increase as larger size particles dominate it. The curing effect takes place to cause the diffusion between particles that result with a larger size of particles as the temperature elevated. However, the size of the particle does not dramatically increase because the particles are in micro-size, which commonly known to have a low surface contact area that hinders the diffusion of particles efficiency although thermal input supplied. This microstructure behaviour contradicted to a nanosized particle where diffusion is more active due to higher surface contact area, hence allowed nanosized particle to dramatically increase in size when exposed to a slight change in temperature [20].

Besides that, under elevated temperature, the microstructure also has a denser structure as the void between particles were reduced. In order to analyses the densification structure of silver, Figure 6 shows a cross-sectional view of silver at room temperature and 120°C. At 120°C, the voids between particles reduced, hence allowed the structure to be denser. This appearance effectively reduces the resistance among the particles as it facilitates the transportation of electron among the silver particles.

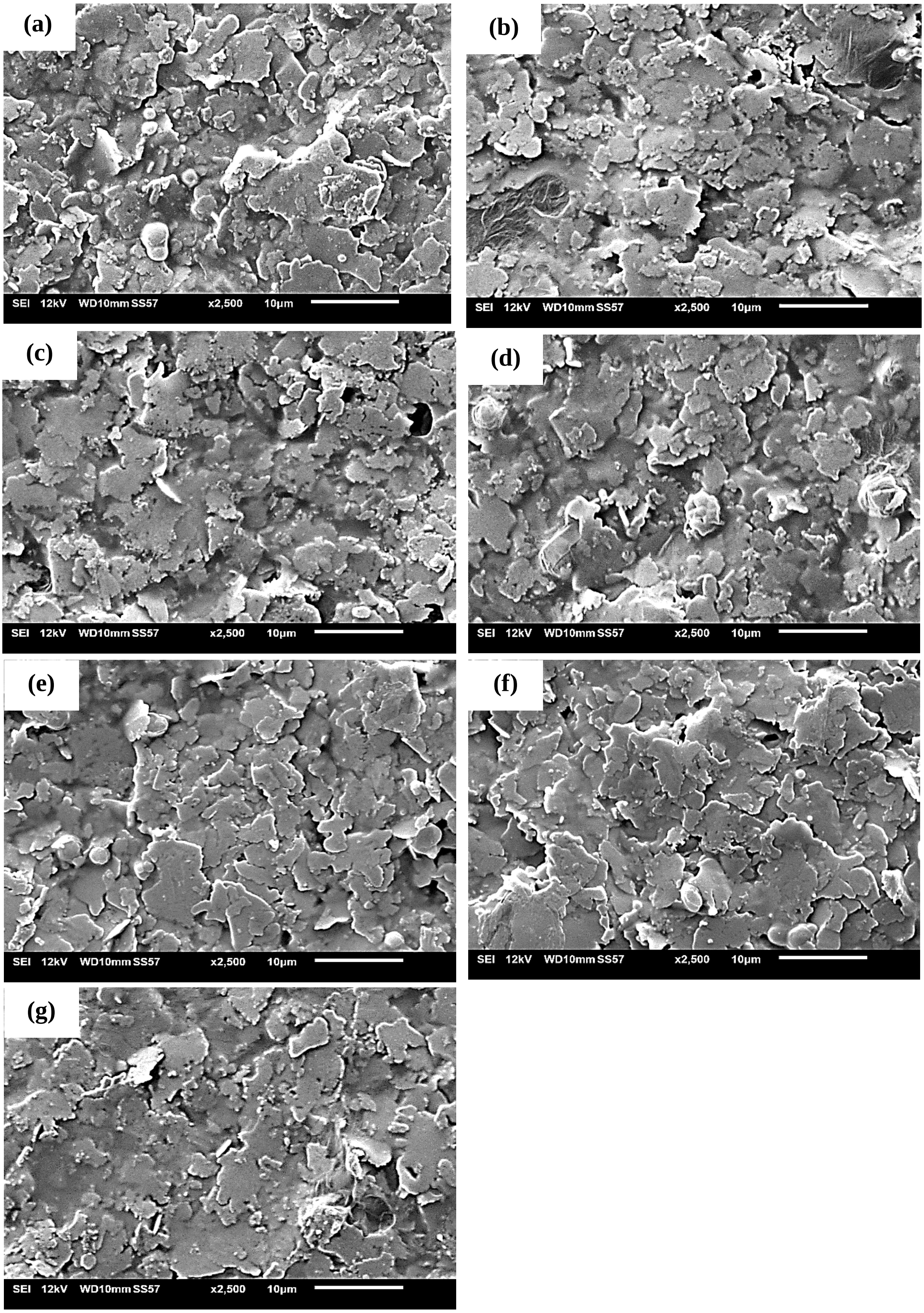

Figure 5 . SEM micrograph of printed silver cured at different temperature: (a) room temperature, (b) 60°C, (c) 80°C, (d) 100°C, (e) 120°C, (f) 130°C, and (g) 140°C.

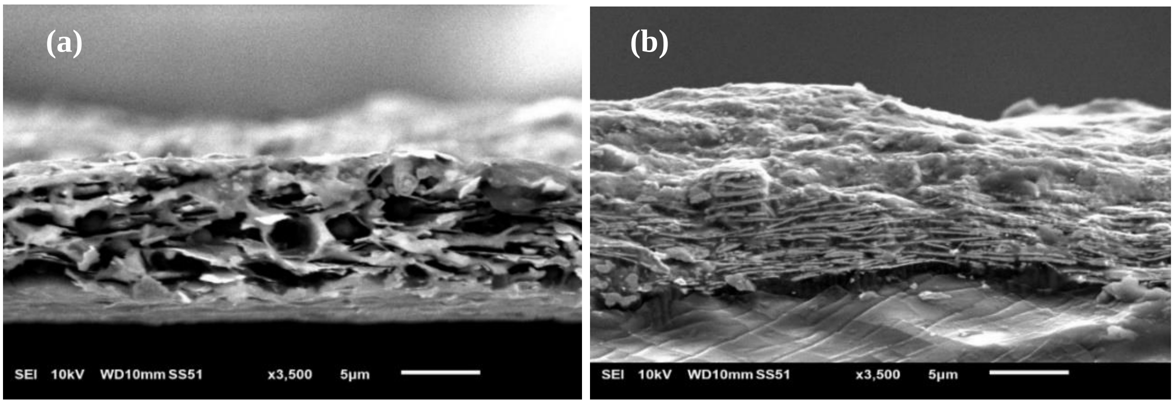

Figure 6. SEM micrograph of a cross-sectional view of printed silver cured at different temperatures: (a) room temperature and (b) 120°C.

Generally, the conductivity performance of silver correlates with the ability of the silver particle to form a denser structure through diffusion routes. The silver particles trigger diffusion routes when exposed to a higher temperature. While these routes take place, the microstructure of particles will undergo disappearing of the grain boundaries, hence lead into larger size silver particle and consequently, resulting in the low mechanical properties of silver. In addition, the bulk diffusion routes allowed the silver to improve their electrical conductivity performance. Nanoindentation analysis was carried out to evaluate the mechanical properties of silver when cured at varies temperature. According to SEM micrograph of silver particles, by curing, high temperature will produce larger particles. The size of silver particles is correlated to mechanical properties. Figure 7 shows the typical load-displacement nanoindentation graph. The depth of nanoindentation is the key for determining mechanical properties of silver. As the temperature increased, the indentation able to penetrate deeper, indicating the hardness reduced with respect to temperature elevation. This result is supported with other work that claims the same reason upon this occurrence [21-23].

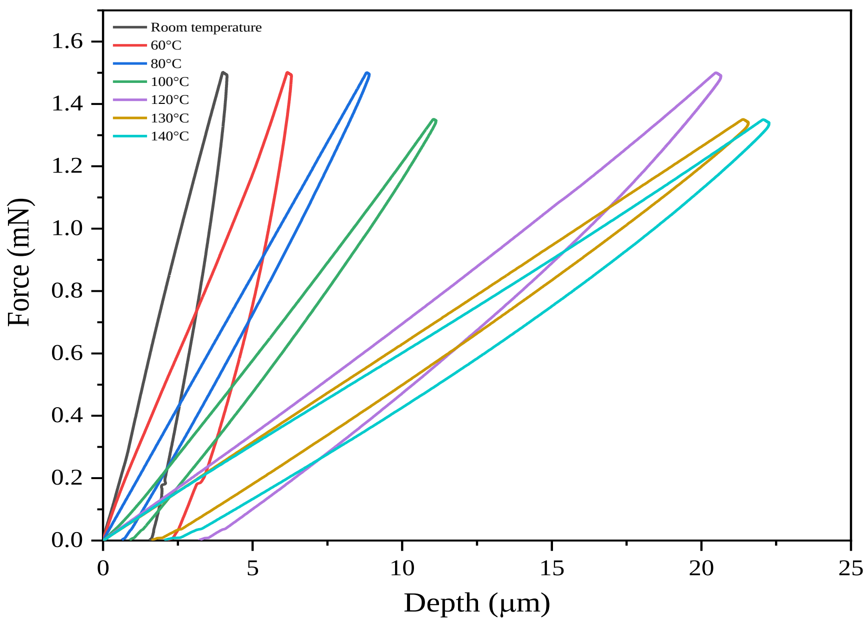

Figure 7. Nanoindentation load-displacement of silver at the different curing temperature.

4. CONCLUSION

Throughout the study, the findings suggest that temperature plays significant roles in determining the electrical conductivity, microstructure and mechanical performance of silver. From the results, it clearly shows that electrical conductivity increases when the temperature increases. This is due to the silver particle start to diffuse with each other when the temperature was increased, hence allowed smooth structure with less void. Therefore, this allows the electron to pass between each other with less resistance. Besides that, the silver also shows low hardness due to the grain boundaries of particles that start to disappear when the temperature increased.

REFERENCES

[1] Basiricò, Laura. Inkjet Printing of Organic Transistor Devices. PhD in Electronic and Computer Engineering. University of Cagliari, (2012)

[2] Yeo, Junyeob, Sukjoon Hong, Daehoo Lee, Nico Hotz, Ming-Tsang Lee, Costas P. Grigoropoulos, & Seung Hwan Ko. Next generation non-vacuum, maskless, low temperature nanoparticle ink laser digital direct metal patterning for a large area flexible electronics, PLoS One, 8 (2012) 1–10.

[3] Son, Yong, Junyeob Yeo, Cheol Woo Ha, Jinhwan Lee, Sukjoon Hong, Koo Hyun Nam, Dong-Yol Yang, & Seung Hwan Ko. Application of the specific thermal properties of Ag nanoparticles to high-resolution metal patterning. Thermochimica Acta, (2012) 52–56.

[4] Fukuda, Kenjiro, Yasunori Takeda, Yudai Yoshimura, Rei Shiwaku, Lam Truc Tran, Tomohito Sekine, Makoto Mizukami, Daisuke Kumaki, & Shizuo Tokito. Fully-printed high-performance organic thin-film transistors and circuitry on one-micron-thick polymer films. Nature Communication, 1 (2014) 1–8.

[5] Walker, S. Brett, & Jennifer A. Lewis. Reactive Silver Inks for Patterning High-Conductivity Features at Mild Temperatures. Journal of the American Chemical Society, 3 (2012) 1419–1421.

[6] Ide, Eiichi, Shinji Angata, Akio Hirose, & Kojiro F. Kobayashi. Metal – metal bonding process using Ag metallo-organic nanoparticles. Acta Materialia, 8 (2005) 2385–2393.

[7] Ko, Seung H., Heng Pan, Costas P. Grigoropoulos, Christine K. Luscombe, Jean MJ Fréchet, & Dimos Poulikakos. All-inkjet-printed flexible electronics fabrication on a polymer substrate by low-temperature high-resolution selective laser sintering of metal nanoparticles. Nanotechnology, 34 (2007) 345202.

[8] Lu, Chun-An, Pang Lin, Hong-Ching Lin, & Sea-Fue Wang. Characterization of the low-curing-temperature silver paste with silver 2-ethylhexanoate addition. Japanese Journal of Applied Physics, (2006) 6987.

[9] Lu, Chun-An, Pang Lin, Hong-Ching Lin, & Sea-Fue Wang. Effects of silver oxide addition on the electrical resistivity and microstructure of low-temperature-curing metallo-organic decomposition silver pastes. Japanese Journal of Applied Physics, 7 (2007) 4179–4183.

[10] Akada, Yusuke, Hiroaki Tatsumi, Takuto Yamaguchi, Akio Hirose, Toshiaki Morita, & Eiichi Ide. Interfacial bonding mechanism using silver metallo-organic nanoparticles to bulk metals and observation of sintering behavior. Materials Transactions, 7 (2008) pp. 1537–1545.

[11] Gao, Jingjing, Rongjun Qu, Bo Tang, Chunhua Wang &, Qianli Ma, and Changmei Sun. Control of the aggregation behavior of silver nanoparticles in polyurethane matrix. Journal of Nanoparticle Research, 10 (2011) 5289–5299.

[12] Tobjörk, Daniel, & Ronald Österbacka. Paper electronics. Advanced Material, 17. (2011) 1935–1961.

[13] Subramanian, Vivek, Josephine B. Chang, Alejandro de la Fuente Vornbrock, Daniel C. Huang, Lakshmi Jagannathan, Frank Liao, Brian Mattis *et al.* Printed electronics for low-cost electronic systems: technology status and application development. ESSCIRC 2008 - Proceedings of the 34th European Solid-State Circuits Conference, (2008) 17–24.

[14] Perelaer, Jolke, Patrick J. Smith, Dario Mager, Daniel Soltman, Steven K. Volkman, Vivek Subramanian, Jan G. Korvink, & Ulrich S. Schubert. Printed electronics: the challenges involved in printing devices, interconnects, and contacts based on inorganic materials. Journal of Materials Chemistry, 39 (2010) 8446.

[15] Perelaer, Jolke, Antonius WM De Laat, Chris E. Hendriks, & Ulrich S. Schubert. Inkjet-printed silver tracks: Low temperature curing and thermal stability investigation. Journal of Material Chemistry, issue 27 (2008) 3209–3215.

[16] Merilampi, Sari, T. Laine-Ma, & Pekka Ruuskanen. The characterization of electrically conductive silver ink patterns on flexible substrates. Microelectronics Reliability, 7 (2009) 782–790.

[17] Greer, Julia R., & Robert A. Street. Thermal cure effects on electrical performance of nanoparticle silver inks. Acta Materilia, 18 (2007) 6345–6349.

[18] Perelaer, Jolke, Chris E. Hendriks, Antonius WM de Laat, & Ulrich S. Schubert. One-step inkjet printing of conductive silver tracks on polymer substrates. Nanotechnology, 16 (2009) 165303.

[19] Nie, Xiaolei, Hong Wang, & Jing Zou. Inkjet printing of silver citrate conductive ink on PET substrate. Applied Surface Science, (2012) 554–560.

[20] Long, Xu, Bo Hu, Yihui Feng, Chao Chang, & Mingyu Li. Correlation of microstructure and constitutive behaviour of sintered silver particles via nanoindentation. International Journal of Mechanical Science, 161 (2019).

[21] Greer, Julia R., & Robert A. Street. Mechanical characterization of solution-derived nanoparticle silver ink thin films. Journal of Applied Physics, 10 (2007) 1–5.

[22] Venkatraman, Ramnath, & John C. Bravman. Separation of film thickness and grain boundary strengthening effects in Al thin films on Si. Journal of Material Research, 8 (1992) 2040–2048.

[23] Nix, William D. Elastic & plastic properties of thin films on substrates: Nanoindentation techniques Material Science and Engineering: A, (1997) 37–44.