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Improving conductivity of rotary screen printed microparticle silver conductors using a roll-to-roll calendering process

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Abstract

A roll-to-roll (R2R) calendering process was developed and used to improve the conductivity of rotary screen printed microparticle silver conductors. Two commercial microparticle silver pastes were used. In the calendering process, the rotary screen printed microparticle silver conductors are compressed under pressure and heat in order to make the porous microparticle layer denser and flatter. The results show that the resistivity of the rotary screen printed microparticle silver conductors was dramatically dropped after the R2R calendering process by 29–56 % depending on the silver paste. The complete drying of the calendered conductor layer decreased the resistivity even further as a result of which the layer resistivity was decreased 74 % from its initial value. The roughness of the silver conductors was also reduced remarkably after the calendering by 45–72 %. The effect of the R2R calendering process on the printed inductively remote readable capacitive moisture sensor based on simple inductor-conductor resonant circuit was also demonstrated. Calendering improved the Q-factor of the sensor but decreased the resonance frequency.

Keywords: rotary screen printing, calendering, microparticle silver, printed conductor, roll-to-roll printing

1. Introduction

Printed large area electronics has been under very active research for past 10 years in various fields in passive (Allen et al., 2011b) – and active electronic (Park et al., 2012) –, optic (Mäkelä and Haatainen, 2012) – and optoelectronic components including organic photovoltaics (Sondergaard et al., 2012) and organic light emitting diodes (Kopola et al., 2009). Despite different printing processes, various other roll-to-roll (R2R) compatible pre- or post-treatment processes are often required to achieve the best performance of the printed electronic components in the R2R manufacturing environment. This is due to a fact that in order to achieve well printable inks they have to include different additives like functional fillers, binder resins, surfactants, wetting agents and/or different boiling point solvents. Typically these additives affect electrical or optoelectronic properties of the printed component. The additives must be removed in order to obtain most efficient component performance.

Conductors in case of electronic circuits play an important role when the performance of the electronic circuit is considered. Resistive losses should be minimized to avoid additional power losses in the circuitry. In addition, physical dimensions and surface properties of the conductors should be optimized in such a way that integration of other components and multilayer structures can be made effectively. Several different processes based on thermal annealing (Girotto et al., 2009), laser sintering (Ko et al., 2007), microwave (Perelaer, de Gans and Schubert, 2006) and electrical sintering (Allen et al., 2011a) as well as chemical (Magdassi et al., 2010) and plasma (Reinhold et al., 2009) sintering have been introduced to reduce the resistivity of the printed nanoparticle silver conductors. It has to be emphasized that these sintering processes work with nanoparticle inks since energy required to sinter nanoparticles is much less than with microparticle based inks.

Calendering is widely used in the common paper making industry to improve the printability of papers by modifying their surface properties. In calendering, the paper is run through one or several nips. The application of compression and heat makes the paper surface denser, smoother, glossier, and flatter. In addition, the texture of the calendering rolls, roll elasticity, and dwell time in the nip affect the final surface properties (Ehrola et al., 1999).

In this paper we introduce a R2R processing technique – calendering – to reduce the resistivity and surface roughness of rotary screen printed microparticle silver conductors. This technique has been previously used to improve the conductivity of printed conductive patterns (Nguyen et al., 2011; Joyce, Fleming and Prabhakar Pandkar, 2010). Recently also a novel pressure-annealing method for fabricating printed low-work-function metal patterns and printed metal alloy patterns was introduced (Yoshida et al., 2011). In addition, an inductively remote readable capacitive moisture sensor based on a simple inductor-capacitor (LC) circuit is manufactured utilizing the rotary screen and R2R calendering processes using real R2R pilot printing machines.

2. Materials and processes

Two commercially available microparticle silver pastes, Asahi LS-411AW and Asahi LS-415C-M, were rotary screen printed with a pilot printing machine, shown in the Figure 1a), onto 125 µm thick and 250 mm wide OPET Lumirror 40.01 plastic foil by Toray. Both inks are one-component, polymer type, microparticle silver pastes whose main difference lies in the viscosity. The viscosities for LS-411AW and LS-415C-M inks are 20–30 Pa s and 30–40 Pa s, respectively. Gallus RVS cylindrical screen with a mesh count of 275 was used to print line patterns having different widths and a inductor-capacitor circuit structure (Figure 2). The inks were printed at a speed of 1 m/min and dried at 140 °C. The total dwell time in the ovens was approximately 4 min.

After the printing, the printed conductor layers were R2R calendered using a thermal nanoimprinting unit of second pilot printing machine, shown in Figure 1b). A smooth and blank nickel sleeve with an anti-adhesion coating was used instead of the imprinting sleeve since the surface texture of the calendering roller is copied onto the surface of the printed layer. The calendering conditions were first optimized with smaller sheets by using different nip pressures (10–15 bar), process speeds (0.5–1 m/min), and cylinder temperatures (110–130 °C). In order to maximize the calendering effects to the printed layers, merely low process speeds and high nip pressures and cylinder temperatures were tested. Finally, the R2R printed LS-411AW and LS-415C-M conductors were calendered in a R2R process using the optimized conditions.

Due to the fact that the conductor layer drying process was extremely short, 4 min, the effect of the complete drying of both printed and calendered layers on the layer properties was also studied. Some samples were dried offline in an oven at 150 °C for 30–60 min. As a result, residual solvents were completely removed.

The printed conductor layers were analysed both before and after the calendering process. The layer thickness and roughness was measured using Veeco Wyko white-light interferometer. In the case of roughness, both R_a (average roughness) and R_q (RMS roughness) values were reported. The ink spreading was measured by determining the line width after the printing and calendering processes with OGP SmartScope video measurement system and OGP MeasureMind metrology software.

a) b)

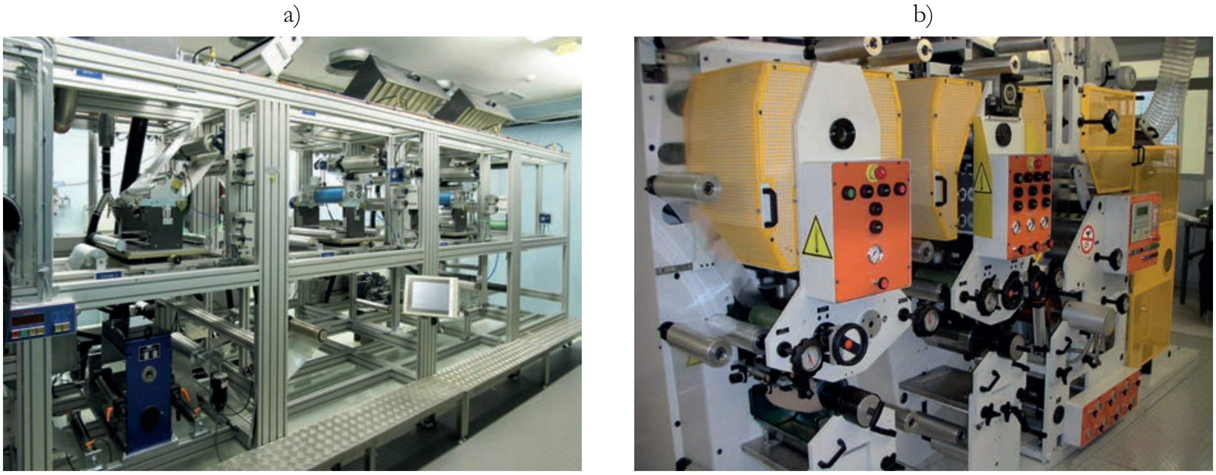


Figure 1: a) Pilot machine used for rotary screen printing of conductive micro-particle pastes and insulator materials; b) Pilot machine used for R2R calendering

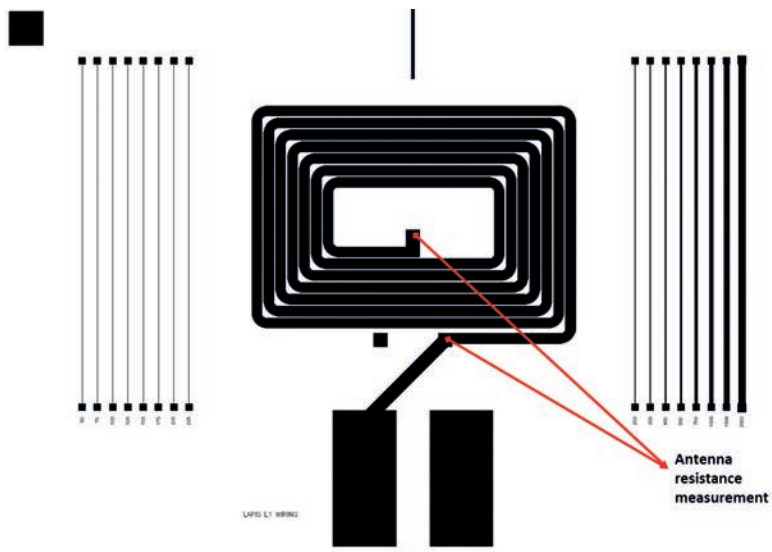


Figure 2: Printing layout containing lines with different widths and a LC-circuit structure in the middle; the resistance across the circuit was measured between the shown points

The layer conductance was determined by measuring the resistance across the antenna (shown in Figure 2 with arrows) and 500 µm wide lines. The volume resistivity (ϱ) of the printed and calendered layers was finally calculated using Equation 1

$$\varrho = RWh/L \quad [1]$$

where means of the line width (W), line length (L), layer thickness (h), and resistance across the line (R) were used.

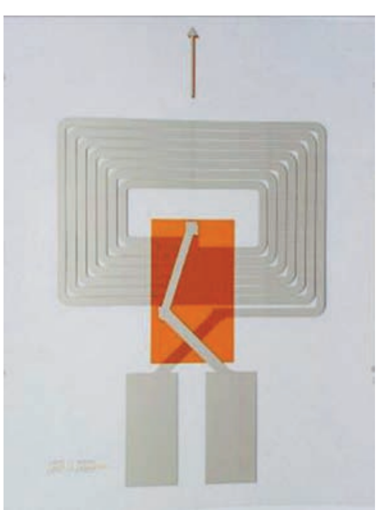


Figure 3: Printed moisture sensor with LC-circuit, dielectric, and wiring layers printed with ROKO printer at a speed of 1 m/min

Moisture sensors design (Hast et al., 2012), shown in Figure 3, was manufactured by screen printing insulator and wiring layers onto the printed LC-circuit. Asahi CR-18Y2-PI(CK) or Asahi CR-18G-KT1 insulators were screen printed onto the LC-circuits after which the wirings were deposited with Asahi LS-411AW silver paste. The two insulating pastes are both two-component type and have similar viscosity of 4–7 Pa s in addition to which their performance was found to be similar, thus making the LC-circuits comparable. Moisture sensors were rotary screen printed at a speed of 1 m/min onto un-calendered LC-circuits. The printed layers were dried at 140 °C and the dwell time in the ovens was 4 min. The insulator layer was printed using Gallus EP cylindrical screen with a mesh count of 110. The insulator layer thickness was 16.1 µm. The wirings were screen printed with Gallus RVS screen (mesh count of 275). In the case of calendered LC-circuits, sensors were printed using a flatbed screen printer and a mesh count of 325. Two layers of insulator were printed in order to obtain similar thickness as in the case of rotary screen printing. After that, the wiring layer was printed. The insulating layer thickness was 16.6 µm. The printed layers were dried in an oven at 140 °C for 4 min (comparable to the R2R process) or at 150 °C for 1 h (complete drying).

The moisture sensor performance was analysed at dry and moist conditions using a measurement setup shown in Figure 4a). Both quality factor (Q-factor) and resonance frequencies were determined using a digital oscilloscope measuring LC-circuit's impulse response and calculating Fast Fourier Transform (FFT) for the measured signal. Q-factor is determined as a ratio of the impulse response resonance frequency (f_0) to 3 dB band width of the impulse response FFT spectrum according to Equation 2. Figure 4b) illustrates definition of the Q-factor in frequency domain.

$$\text{Q-factor} = f_0/f_{3dB} \quad [2]$$

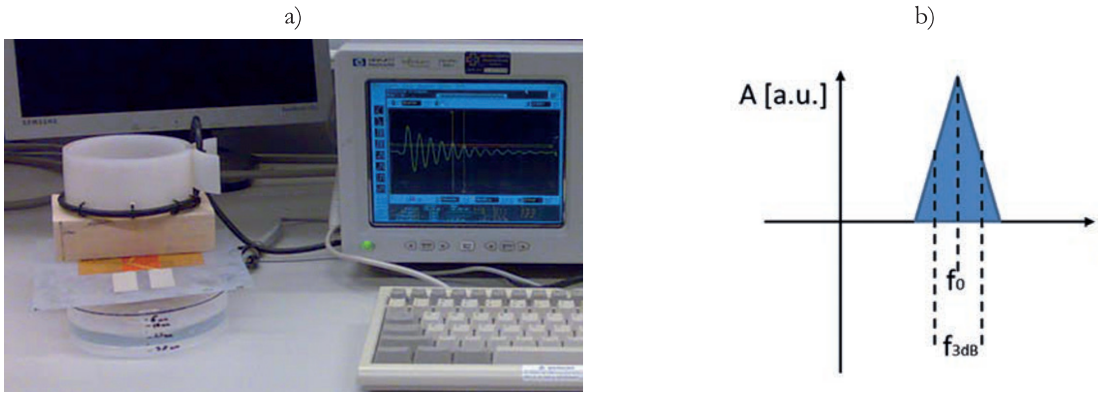


Figure 4: a) Measurement setup for the analysis of the resonance frequencies and Q-values of the printed sensors at moist and dry conditions; the sensor is separated from the water source by 4 cm thick dry Finnish pine wood; b) Definition of Q-factor in frequency domain

3. Results and discussion

3.1 Effect of calendering on the surface properties of the printed layer

The optimum R2R calendering conditions were first determined by feeding R2R printed sheets into the process. Figure 5 and Figure 6 show the results. Calendering increases the layer conductivity by making the layer smoother and denser. As a result, silver particles in the ink layer are compressed into more intimate contact with each other and the amount and size of empty spaces in the layer decrease. This allows less resistive current flow through the layer. The resistance across the antenna decreases 40–55 % during the calendering and the amount depends on the calendering conditions and ink type and printed layer properties.

The increase in the calendering nip pressure has no significant effect on the conductivity. This resulted from the limit of the nip pressure beyond which the ink layer cannot be compressed anymore. Furthermore, too high nip pressure can also cause damages to the printed layer or lead to the ink sticking onto the calendering sleeve. Therefore, the nip pressure level of 10 bar was chosen for the R2R calendering experiments.

As the calendering speed decreases from 1 m/min to 0.5 m/min, the dwell time of the ink layer in the nip under compression increases, thus fortifying the calendering effects to the printed layers. This leads to smoother, denser, more even, and more conductive layers. The conductivity of the ink layer increases approximately 5 %.

The increase in the calendering temperature by 10 °C also improves the layer conductivity by 10 %. The higher the calendering temperature, the softer and more easily deformable the ink layer gets. However, if the calendering temperature is increased excessively, binders in the ink become sticky. This leads to the fouling of the calendering sleeve and causes damages to the ink layer.

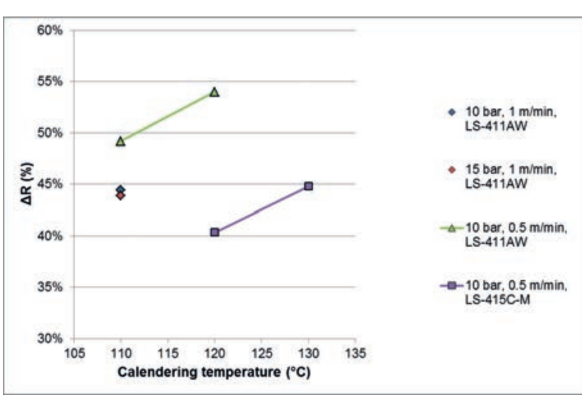


Figure 5: Antenna resistance changes ($\Delta R(\%) = (R_{initial} - R_{calandered})/R_{initial}$) of printed Asahi LS-411AW and LS-415C-M sheets during R2R calendering using different calendering temperatures, speeds, and pressures

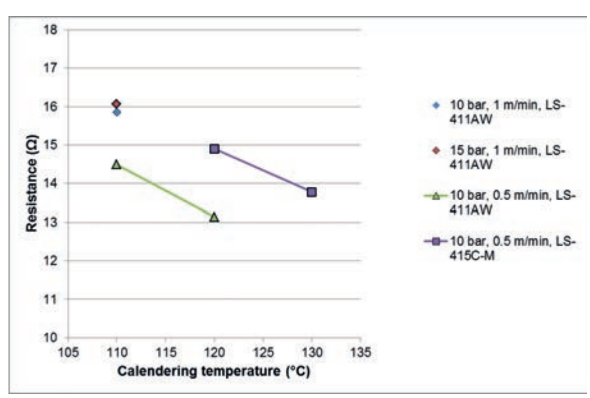


Figure 6: Resistance across the printed LC-circuit sheets after R2R calendering as a function of calendering temperature, speed, and pressure. Both Asahi LS-411AW and LS-415C-M inks are used

LS-415C-M ink layer does not respond to the calendering as well as LS-411AW ink. Un-calendered LS-415C-M ink layers are more conductive than LS-411AW ink layers but after calendering LS-411AW layers become more conductive. For example, calendering at 120 °C increases the conductivity by 54 % in the case of LS-411AW ink and only 40 % in the case of LS-415C-M ink.

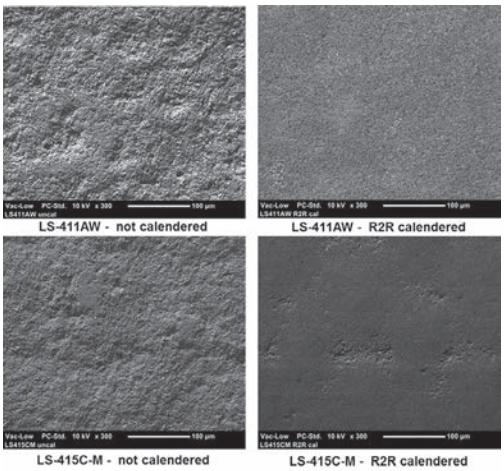


Figure 7: Effect of the ink type and R2R calendering on the surface properties of the conductor layer; images are taken with SEM using a magnification of ×300

The R2R calendering experiments were done for both conductor inks using a calendering speed of 0.5 m/min and temperature of 120 °C. In Figure 7, the effect of the R2R calendering on the layer topography is shown. The calendering process makes the printed layers significantly smoother and more uniform because of the heat and compression encountered in the nip. The irregularities of the ink layer surfaces disappear and the ink layer becomes denser, thus making better and more intimate particle-to-particle contacts. Initially, LS-415C-M conductor layer is smoother than LS-411AW conductor layer but after the calendering process the irregularities of the layer printed with LS-411AW ink have evened out better. Thus, LS-411AW ink layer is more conformable.

After printing LS-411AW ink layers are thicker and they spread more than LS-415C-M layers due to the lower viscosity of LS-411AW ink. The lower the viscosity, the more the ink is squeezed through the tiny holes of the screen, i.e. is transferred onto the substrate. At the same time, the ink spreading also increases. LS-415C-M ink produces also smoother layers than LS-411AW ink.

The thickness, roughness, and ink spreading changes during calendering are presented in Figure 8a, Figure 8b, and Table 1, respectively. The R2R calendering decreases the layer thickness and roughness, and slightly increases spreading. However, LS-415C-M ink layers do not respond to the calendering as well as LS-411AW ink layers because of the thinner layers and higher solids content of the ink. The thinner the layer, the less it can physically be compressed and deformed. In addition, the higher solids content decreases the amount of empty space in the ink layer, thus decreasing the layer response to the calendering.

In calendering, the printed layer is densified since empty spaces in the printed layer are removed and particles in the ink layer get into better contact with each other. This decreases the layer thickness by 21 % and 13 % in the case of LS-411AW and LS-415C-M inks, respectively. However, the ink spreading increases only 1–2 % during the calendering. This is caused by the fact that the ink layer entering the calendering process is almost dry and it is only softened in the nip. Therefore, the short dwell time in the nip is not enough to make the ink flow on the substrate.

Table 1: Spreading of Asahi LS-411AW and LS-415C-M inks during R2R calendering

Ink	Spreading of 500 µm lines (µm)	
	Before	After
LS-411AW	36	46
LS-415C-M	3	8

a) b)

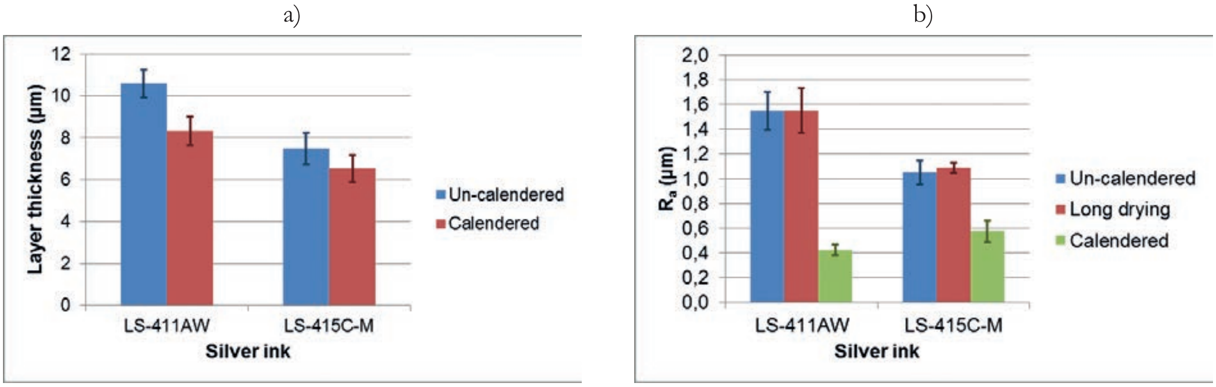


Figure 8: Effect of the calendering on the layer thickness (a) and average layer roughness (b) in the case of Asahi LS-411AW and Asahi LS-415C-M silver pastes; the effect of the further oven drying on the layer roughness is also presented

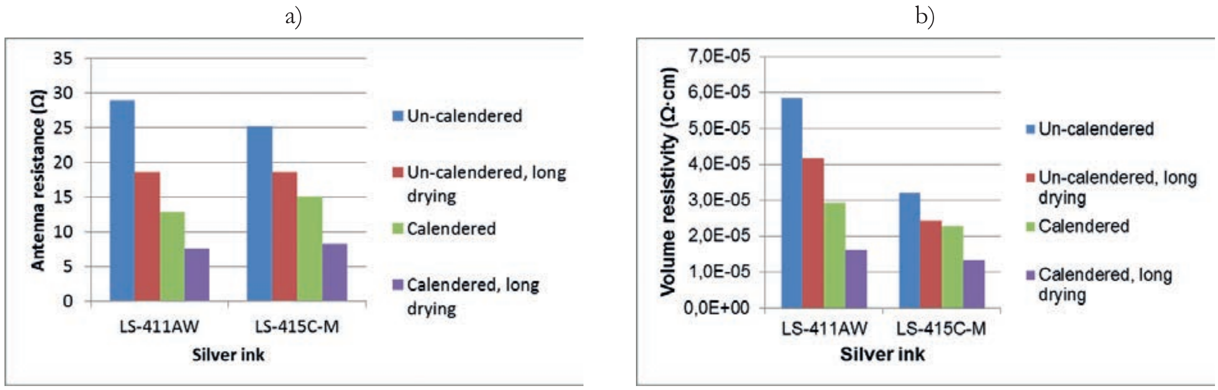


Figure 9: Effect of the calendering and extra oven drying on the LC-circuit resistance (a) and volume resistivity (b) in the case of Asahi LS-411AW and Asahi LS-415C-M silver pastes

The ink layer roughness decreases 72 % during calendering of LS-411AW ink layers. The smoothness of LS-415C-M layers increases 45 %. The smooth metal sleeve surface is copied onto the surface of the printed layer and the ink layer is compressed, thus removing the surface irregularities. The extra oven drying step alone does not affect the layer roughness since only small amount of residual solvents are removed from the ink layer and no mechanical action is caused to the ink layer.

On the other hand, the maximization of the ink layer drying process is highly important in the formation of the layer conductivity, as illustrated in Figure 9. Without calendering, the layer conductivity can be improved 26–36 % by merely drying the printed layers completely. The complete drying of the calendered layer increases the conductance by 40–45 %. In the best case scenario, the optimization of the both calendering and drying parameters can increase the printed layer conductance even by up to 74 %.

R2R calendering can improve the surface properties and conductivity significantly. This typically enhances also the deposition process and surface properties of the subsequently deposited layers as well as the electrical performance of the final devices. Layer smoothness ensures that subsequent layers are easily deposited and they have uniform properties whereas conductivity affects mostly the device performance by enhancing current flow. The properties of the printed layers are typically improved by changing the ink properties and behaviour on the substrate but this often leads to significant changes in the ink spreading, i.e. the detail rendering. Calendering, for its part, can improve surface properties of the printed layer without affecting the ink spreading behaviour. The response of the ink layer to the calendering action depends heavily on the ink layer composition. The ink layer has to contain binders and be compressible to allow proper calendering effects. However, too thin or plain metal layers are not necessarily deformable in the calendering nip. In addition, sintered metal particles might have lost their compressibility. In addition to the calendering process, it is highly important to optimize the drying of the ink layer to maximize its electrical performance.

3.2 Effect of the calendering on the performance of the R2R printed moisture sensor

The printed moisture sensors are sensitive to the changes in the moisture content, as seen in Figure 10 and Figure 11. As the moisture content increases, both the resonance frequency and Q-factor decrease by 7 % and 10 %, respectively. The Q-factor is rather low (4.9–5.6) when the LC-circuit is not calendered, thus making the reading distance small. In this study, the reading distance was 4 cm. Calendering of the LC-circuit increases the Q-factor by 19 % to 6.0–6.5, thus making the moisture sensor performance better. However, at the same time the resonance frequency decreases from 10.24–11.12 MHz to 9.73–10.36 MHz.

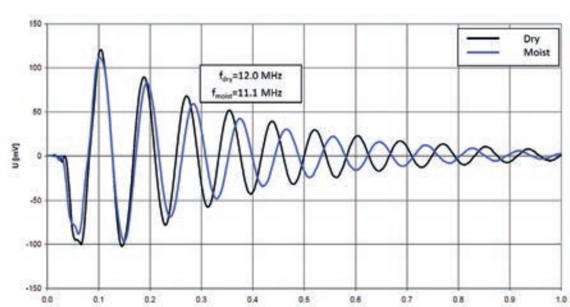
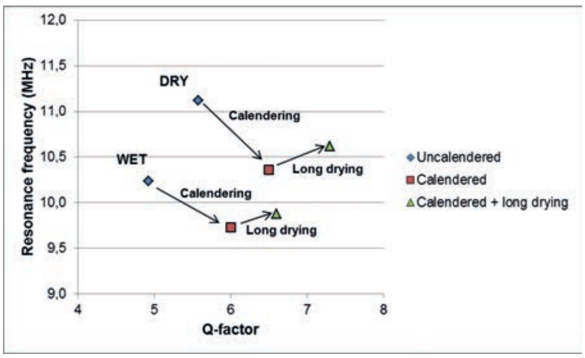


Figure 10: Resonance behaviour of a printed moisture sensor at dry and moist conditions. LS-411AW was the conductor material and CR-18Y2-PI(CK) was the dielectric material.

This might cause problems in the reading process of the sensor since the readers work typically only at a certain frequency. It was found that the resonance frequency can be adjusted by changing the sensor layout without affecting the Q-factor. The complete drying of the printed layers improves also the sensor performance by increasing the Q-factor by 11 % to 6.6–7.3. The resonance frequency increases slightly. LS-415C-M ink gives poorer moisture sensor performance than LS-411AW ink when the LC -circuit layers are calendered. However, when the conductor layers are completely dried the differences between these two inks disappear.

a)



b)

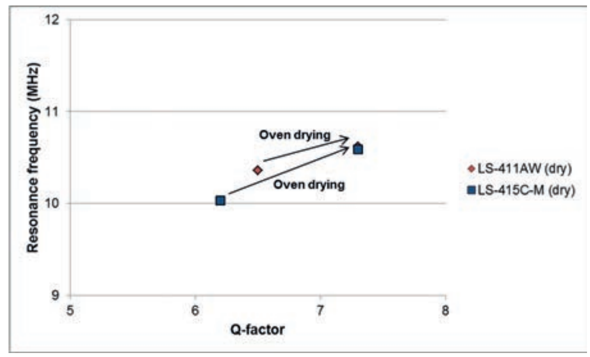


Figure 11: a) Resonance frequencies and Q-factors of the moisture sensors as a function of calendering, long oven drying, and moisture content; under wet environment, the resonance frequencies and Q-factors are lower; b) Effect of the ink type on the Q-factor of the printed moisture sensors; the LC-circuit layer was calendered in R2R process

4. Conclusions

R2R calendering process for rotary screen printed microparticle silver conductor layers was developed and optimized using real R2R pilot printing machines. The calendering improved the layer smoothness and conductivity significantly by compressing the conductor layers. Smooth surface of the calendering sleeve ensured the large smoothening of the printed layer whereas the compression forced metal particles closer to each other by densifying the layer. Low calendering speeds and high calendering temperatures were beneficial for the final properties of the conductor layers. In addition to the calendering, the complete drying of the ink layer maximized the layer conductivity. The calendering was also utilized in the R2R printing of inductively remote readable capacitive moisture sensor and it improved the moisture sensor's performance. The calendering process is very simple and it can be implemented easily to the printing machine construction. It offers an affordable way to improve the conductivity and reduce the layer thickness in the rotary screen printing process of microparticle silver pastes.

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References

Allen, M., Alastalo, A., Suhonen, M., Mattila, T., Leppäniemi, J. and Seppa, H., 2011a. Contactless electrical sintering of silver nanoparticles on flexible substrates. *IEEE T. Microw. Theory*, Vol. 59, pp. 1419–1429.

Allen, M., Lee, C., Ahn, B., Kololuoma, T., Shin, K. and Ko, S., 2011b. R2R gravure and inkjet printed RF resonant tag. *Microelectron. Eng.*, Vol. 88, pp. 3293–3299.

Ehrola, J., Hernesniemi, A., Kuosa, H., Kyytsönen, M., Linnonmaa, P., Mäenpää, T., Pietikäinen, R., Staples, R. and Vuorikari, H. 1999. Calendering. In Jokio, M. (ed.), *Papermaking Science and Technology: Papermaking Part 3, Finishing*. Fapet Oy, Jyväskylä. pp. 14–140.

Girotto, D., Rand, B., Steudel, S., Genoe, J. and Heremans, P., 2009. Nanoparticle-based, spray-coated silver top contacts for efficient polymer solar cells. *Org. Electron.*, Vol. 10, pp. 735–740.

Hast, J., Jansson, E., Petäjä, J., Honkala, J., Häkkinen, J., 2012. Roll-to-Roll Printing of Inductively Readable Capacitive Moisture Sensors. *8th International Conference on Organic Electronics (ICOE12)*, Tarragona, Spain.

Joyce, M., Fleming, P. and Prabhakar Pandkar, S., 2010. Flynn Thiel Boutell & Tanis, RC. *Method of improving the electrical conductivity of a conductive ink trace pattern and system thereof.* Pat. US 2010/0231672.

Ko, S., Pan, H., Grigoropoulos, C., Luscombe, C., Fréchet, J.M. and Poulikakos, D., 2007. Air stable high resolution organic transistors by selective laser sintering of ink-jet printed metal nanoparticles. *Appl. Phys. Lett.*, Vol. 90, p. 141103.

Kopola, P., Tuomikoski, M., Suhonen, R. and Maaninen, A., 2009. Gravure printed organic light emitting diodes for lighting applications. *Thin Solid Films*, Vol. 517, pp. 5757–5762.

Magdassi, S., Grouchko, M., Berezin, O. and Kamyshny, A., 2010. Triggering the sintering of silver nanoparticles at room temperature. *ACS Nano*, Vol. 4, pp. 1943–1948.

Mäkelä, T. and Haatainen, T., 2012. Roll-to-roll pilot nanoimprinting process for backlight devices. *Microelectron. Eng.*, Vol. 97, pp. 89–91.

Nguyen, H., Hoang, N., Shin, K.-H. and Lee, S., 2011. Improvement of surface roughness and conductivity by calendering process for printed electronics. *8th International Conference on Ubiquitous Robots and Ambient Intelligence (URAI)*, Incheon, Korea, pp. 685–687.

Park, H., Kang, H., Lee, Y., Park, Y., Noh, J. and Cho G., 2012. Fully roll-to-roll gravure printed rectenna on plastic foils for wireless power transmission at 13.56 MHz. *Nanotechnology*, Vol. 23, 344006.

Perelaer, J., de Gans, B.-J. and Schubert, U.S., 2006. Ink-jet printing and microwave sintering of conductive silver tracks. *Adv. Mater.*, Vol. 18, pp. 2101–2104.

Reinhold, I., Hendricks, C.E., Eckardt, J.M., Kranenburg, R., Perelaer, J., Baumann, R.R. and Schubert, U.S., 2009. Argon plasma sintering of inkjet printed silver tracks on polymer substrates. *J. Mater. Chem.*, Vol. 19, pp. 3384–3388.

Sondergaard, R., Hösel, M., Angmo, D., Larsen-Olsen, T.T. and Krebs F.C., 2012. Roll-to-roll fabrication of polymer solar cells. *Mater. Today*, Vol. 15, pp. 36–49.

Yoshida, M., Suemori, K., Uemura, S., Hoshino, S., Takada, N., Kodzasa, T. and Kamata, T., 2011. Printed electrode for all-printed polymer diode. *Jpn. J. Appl. Phys.*, Vol. 50, p. 04DK16.