Inkjet printing technology and conductive inks synthesis for microfabrication techniques

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Abstract
Inkjet printing is an advanced technique which reliably reproduces text, images and photos on paper and some other substrates by desktop printers and is now used in the field of materials deposition. This interest in maskless materials deposition is coupled with the development of microfabrication techniques for the realization of circuits or patterns on flexible substrates for which printing techniques are of primary interest. This paper is a review of some results obtained in inkjet printing technology to develop microfabrication techniques at Laboratory for Nanotechnology (LNT). Ink development, in particular conductive ink, study of printed patterns, as well as application of these to the realization of radio-frequency identification (RFID) tags on flexible substrates, are presented.

Keywords: inkjet printing, silver nanoparticles ink, copper nanoparticles ink, microfabrication techniques, antenna, RFID tag

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1. Introduction

Drop-on-demand inkjet technology developed over the last 30 years as a means of achieving an efficient means of consumer printing. At present, this non-contact technology has reached such a quality that it allows printing photography with unsurpassed quality. The specific advantage of this technology is its ability to print a controlled amount of ink, down to 1 pl, at high frequency, on almost any type of substrate. Thanks to developments of the technology for consumer purposes, it is now possible to use it for the deposition of materials on any surface. In the past decades, such developments progressed and demonstrations were made in many directions, including the deposition of electrical circuits [1], organic and inorganic transistors [2, 3], coatings for liquid crystal displays (LCDs) [4], biological cells [5], solar cells [6], etc.

Nevertheless, the process of ejecting droplets from a nozzle and of the ink spreading and drying on a substrate is a complex one. The ejection first needs to overcome the surface tension holding the liquid in the nozzle. Desktop printers are essentially based on the thermal drop-on-demand principle. As the material to be printed, the drop-on-demand piezoelectric one is preferred because it avoids the risk of damaging or modifying this material during the printing process. The breakup mechanism at ejection is most often accompanied with the generation of small unwanted droplets called satellites [7]. Then the impact on the substrate is also key to the final deposited pattern as the spreading, while also controlled by the wettability of the ink on the substrate, is dependent on the kinetic energy of the droplet as well as its viscosity [8]. The study of these phenomena is a key aspect of inkjet technology to reach high level of accuracy on the printed patterns.

These fundamental and applied aspects of inkjet printing are the focus of the on-going research at the Laboratory...
for Nanotechnology (LNT). The present paper is aimed at reviewing some of the work and results obtained so far in conductive ink development, printed pattern analysis as well as application of inkjet printing to the fabrication of RFID tags on flexible plastic foils [9,10].

2. Conductive ink developments

2.1. General considerations about conductive nanoparticle based inks

The ink is the core of the technology because all final material properties as well as drawbacks are dictated by its chemistry. To name a few, the evaporation, the film homogeneity, the electrical properties, all rely heavily on ink formulation. In this sense one ink formulation would probably not fit all applications. For conductive ink the most widely used material is silver nanoparticles dispersed in an appropriate carrier which allows for proper ink ejection control. This situation also implies that control of the nanoparticles synthesis is important for the ink development. This study also includes the compatibility of the solvent with the particles as well as the choice of a suitable formulation for the nanoparticles carrier. In an effort to bring down the cost of conductive inkjet printing, LNT also developed a copper nanoparticles ink. This material is ideal, but obtaining an ink with it faces the difficulty of its rapid oxidation in ambient atmosphere. Therefore studies at LNT are underway to control the surface of the particles in order to reach a low resistivity of the final thin film while keeping the advantage of the low cost of this material.

2.2. Metal nanoparticles synthesis

2.2.1. Silver nanoparticles synthesis. In a typical procedure, an appropriate amount of polyvinylpyrrolidone (PVP) was dissolved in 20 ml ethylene glycol (EG). Next, AgNO₃ was added into the above solution. Then, an ultrasonic probe was immersed into the mixture solution for 3 min. Upon the start of the reaction, the pale yellow solution changed to dark brown, indicating the formation of silver particles. The silver concentration in the synthesized solutions was 9.5 wt%. At this high concentration the solution is viscous and there is the necessity to dilute it for the various analyses. This was done in ethanol with a gentle ultrasonic dispersion (figure 1).

The shape and size distribution of colloidal particles were characterized by transmission electron microscopy (TEM) 2 days after preparation. Figure 2 shows a TEM image and the computed size distribution of colloidal silver particles. The mean diameter of the spherical silver nanoparticles is 10 nm with a narrow distribution ranging from 4 to 16 nm.

Synthesized samples were also studied by ultraviolet–visible (UV–Vis) absorption spectroscopy from a double-beam spectrophotometer (Varian Cary 100) in the wavelength range from 190 to 1100 nm. Figure 3 shows the UV–Vis spectra of silver colloids of the synthesized solutions. As is clearly seen, the optical absorbance appears at a wavelength of 409 nm, which relates to the surface plasmon resonance of silver nanoparticles [11].

2.2.2. Copper nanoparticles synthesis. Ascorbic acid solution was prepared by dissolving 52.8 mg in 15 ml of ethylene glycol. A solution of copper (II) sulfate pentahydrate, CuSO₄·5H₂O (0.01 M) in ethylene glycol was separately prepared and this solution was added to the solution of ascorbic acid under strong magnetic stirring. Various amounts of PVP were then added to explore its influence on nanoparticle size. Then a solution of NaOH (1 M) in ethylene glycol was added dropwise to adjust the pH up to 12. After stirring at room temperature for about 1 h, a solution of NaBH₄ (0.1 M) in ethylene glycol was added to the mixture under continuous strong stirring for about 10 min. The initial blue color of the reaction mixture turned yellow and eventually light red.
A UV–Vis absorption spectrum of Cu nanoparticles is shown in figure 4. The absorption bands for Cu nanoparticles have been reported to be in the range of 500–600 nm [12]. As is clearly seen, a local maximum of the optical absorbance appears at a wavelength 561 nm, which is related to the surface plasmon resonance of copper nanoparticles.

The surfactants agent (PVP) can form an absorption layer at the surface of the copper nanoparticles to prevent the particles aggregating by increasing the repulsion force between the particles. Figure 5 shows the TEM images for colloidal Cu nanoparticles synthesized and the histogram of the particle size distribution. The particles are spherical with some trend toward aggregation. We can see in the picture that the mean diameter of copper nanoparticles is about 45 nm with a much wider size distribution than for silver nanoparticles.

While synthesizing and using copper nanoparticles, the main problem is that they are easily oxidized. Even a very thin surface oxide layer can significantly affect their physical and chemical properties. Therefore, synthesis of copper nanoparticles and conductive ink formulations require optimal protection of copper nanoparticles not only against aggregation but against oxidation as well.

As is well known for silver nanoparticles the capping agent (PVP), which helps Cu nanoparticles to avoid aggregation, can also protect them against oxidation by markedly decreasing the oxidation rate. Addition of antioxidants, such as ascorbic acid, was shown to also retard the rate of Cu nanoparticle oxidation. To study the stability of the nanoparticles, the surface plasmon resonance of colloid copper nanoparticles was measured immediately after synthesis, 2h, 4h, 3 days and 22 days from sample preparation (figure 6). The surface plasmon resonance does not markedly change during the 3 days after preparation. A slight change is observed after 22 days with a shift of the resonance to 547 nm (from the spectrum shown in the inset of figure 6). Furthermore the solution was confirmed to be stable even after 2 months.
Table 1. Formulation of metal nanoparticles ink.

|                   | Ethyleneglycol (wt%) | 2-methoxyethanol (wt%) | Methanol (wt%) | Ethanol (wt%) | Glycerin (wt%) | 2-isoproxyethanol (wt%) |
|-------------------|----------------------|------------------------|----------------|--------------|---------------|------------------------|
| Silver nanoparticles ink (20 wt%) | 32                    | –                      | –              | 32           | 4.8           | 11.2                   |
| Copper nanoparticles ink (0.1 wt%) | 70                    | 19.9                   | 10             |

2.3. Ink formulation and properties

Optimization of the metal (copper and silver) nanoparticles synthesis (particle size, stabilization) is one of the crucial points in obtaining inks for printing patterns with high electrical conductivity. Inks based on the metal nanoparticles were prepared by dispersing the metal nanoparticles in the form of powder into organic solvent with proportions as in Table 1. Subsequently, the mixture was dispersed for approximately 10 min.

After the preparation of the silver nanoparticles ink, the ink particles were observed using a TEM. Figure 7(a) and 7(b) show a TEM image and the computed histogram of particle size distribution of these particles. The figure clearly shows that the particles are well separated and spherical, the average diameter of silver nanoparticles being about 5 nm with a narrow distribution. The UV–Vis absorption spectra of silver nanoparticles ink is shown in figure 7(c). As is clearly seen, the maximum of the optical absorbance appears at a wavelength 407 nm.

The ink bears many roles in inkjet printing, including the possibility to eject droplets through a nozzle. Material to be printed is mainly the drop-on-demand piezoelectric material. To obtain a good jetting, the ink should have controlled surface tension as well as viscosity. The silver nanoparticles ink has a measured viscosity of 12.1 cP and a surface tension of 29.5 mN m$^{-1}$ at metallic silver concentrations of 20 wt%, indicating that an ink composed of silver nanoparticles has been successfully prepared.

In figure 8, the newly-prepared ink has a plasmon resonance peak at 596 nm, which proves that the copper nanoparticles are stable in the solution. The copper ink in this study has a measured viscosity of 13.5 cP and surface tension of 42.3 mN m$^{-1}$ at a metallic copper concentration of 0.1 wt%. This result is compatible with our inkjet equipment for later applications.

Once the ink is firmly stable itself, and its jetting is also well controlled, an important aspect is the interaction of the droplet with the substrate, i.e. spreading, as well as the solvent evaporation. In the case of nanoparticles-based inks there is also a subsequent need for consolidation of the deposit through annealing.

3. Three-dimensional shape of printed lines

An important characteristic of most inks is the presence of a solvent which evaporates after the droplet has spread on the substrate. The solute of the ink, the material that is of interest at the end of the deposition process, is moved inside the drying droplet as a consequence of the evaporation. For most cases where the droplet has a contact angle to the substrate below 90°, the evaporation rate is higher at the contact line and the solute is moved in the direction of this contact line. This movement is the cause of the coffee stain effect. But the goal in most ink deposition is to obtain a smooth profile of the final
deposit and not a concentration of the materials at the edge of the printed patterns. Therefore, specific control has to be applied in order to obtain such smooth deposit.

For application to printed electrical circuits, the nanoparticles-based ink is the most suitable since it can be annealed at low temperature which allows printing on almost any kind of substrate. For the results presented in this section we used commercial ink (Sunjet U5603). This ink was used to print straight lines with a Dimatix printer (2800 series) on poly(ethylene terephthalate) (PET) and silicon, the first being a cheap commercial film and the second being interesting for its surface smoothness and good thermal conductivity. Lines were printed at drop spacing from 5 to 60 µm by increment of 5 µm. The line cross section profiles were measured by a confocal microscope (Sensofar).

Beyond the fact that the spreading of the ink on any substrate is controlled by its wettability, two main results are interesting with regard to controlling the line cross section profile. We show that (i) it is possible to predict the line width and cross section area by simply measuring them on a line printed at low drop spacing; (ii) the substrate thermal conductivity impacts the evaporation step which influences the final cross section profile.

Figure 9 shows the cross section profiles of lines printed on PET and silicon at 50 °C. On PET, for large drop spacing (just at the time the droplets merge in a line), there is a central recess with side peaks. As the drop spacing is decreased, the central recess disappears and the top of the line is flat. When the drop spacing decreases further there is a reappearance of the central recess. Figure 10 shows at which conditions (drop spacing and substrate temperature) the profile top is flat on PET (black dots). This always happens at large drop spacing. It is attributed to the fact that PET has a low thermal conductivity which leads to long evaporation step. This gives more time for nanoparticles to be drained toward the edges of the line. Only in a given temperature range and when the line volume is small (large drop spacing) is there a possible balance leading to flat profile top.

On silicon, the situation is different as is visible in figure 9(b). The profile is concave (with a recess) then flat with a central peak, then convex, flat again and concave again. Silicon has a much higher thermal conductivity which leads to faster evaporation. At the same time the contact angle of the ink on silicon is much smaller than on PET (∼20° compared to ∼40°). This leads to higher evaporation rate at the contact line. The evaporation dynamics is therefore quite different, which leads to a very different situation for the cross section profile of lines.

Now a simple geometrical model [13,14] indicates that the cross section area evolves as the inverse of the drop spacing while the line width evolves as the inverse of the

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**Figure 8.** UV–Vis spectrum of the copper nanoparticles ink and image of the fresh copper nanoparticles ink.

**Figure 9.** Cross section profiles at different drop spacing (expressed in µm) for lines printed on (a) silicon and (b) PET.

**Figure 10.** Occurrence of flat profile top for lines printed on PET at different drop spacing and substrate temperature.
The agreement of the measurements with the model demonstrates that it is readily possible to predict the behavior of an ink on a given substrate just by measuring the section profile of a line printed at the smallest drop spacing. This is an interesting observation, useful to speed up the exploration of the printing behavior of a given ink on various substrates.

4. Antenna processing

In this application the conductive ink is used for printing a seed layer for the antenna structures (figure 12(a)). The cartridge used consists of 16 nozzles with 10 pl drop volume (DMCLCP-11610). Print parameters were optimized first, including the distance between the printhead and the substrate, the temperature of the substrate, the drop spacing and the waveform profile to actuate the nozzles. RFID antennas were printed using the same commercial silver ink (U5603). This ink is a silver nanoparticles solution containing 20 wt% of metal silver particles with a mean diameter slightly less than 30 nm. During the printing process, the distance between the printhead and the substrate was maintained at 1 mm and the substrate heated and maintained at 60 °C. The optimal values of droplet spacing in both X- and Y-directions were found to be 20 µm. These optimized parameters were used for all the experiments.

After the printing of the antenna, it is essential to cure the layer in order to remove excess solvent and increase the conductivity of the silver ink [15]. The curing process also provides the benefit of increasing the adhesion of silver ink patterns on PET substrate. Figure 13 shows the
difference between heating temperature 100 and 150 ⁰C. At lower temperature, the particles do not look connected. When the temperature is increased to 150 ⁰C, the particles start to coalesce, which is visible through the necking between adjacent particles. Curing temperature of 150 ⁰C is used in the following fabrication to sufficiently cure the nanoparticles ink.

To increase the thickness of the deposit and reduce the sheet resistance, it is possible to use multiple layer printing. However, the resistivity of the inkjet printed thin film tends to be much higher than the bulk metal [15]. As an alternative method, an electrodeposition copper plating process is performed for which printed silver nanoparticles patterns form the seed layer for growth of a metal thick film (figure 12(b)). The resistance of copper deposition can be determined by the four-point prober. At least two samples are prepared for each plating time, and thickness and at least five different positions for each sample are measured. The average of the thickness for each plating time is given in figure 14. The thickness of copper deposition linearly increases along with the plating time. The growth rate of the deposited copper thickness during the electrodeposition plating is about 8.8 nm min⁻¹. As expected, the resistance decreases along with the plating time. Sheet resistances as low as 2.6 × 10⁻³ Ω square⁻¹ were obtained at a copper film of about 10.2 μm (after 80 min of deposition).

5. Conclusion

The development of conductive inks based on nanoparticles has progressed at the LNT over the past 2 years. Capacity was developed and a first level silver ink formulated which is currently under test. The problems in formulating a conductive ink are multiple. We are especially focusing our efforts on ensuring a stable concentrated ink as the colloidal inks tend to destabilize at high concentration. From a practical point of view this is a key step, since a highly concentrated ink is more effective in printing speed as it avoids multipass to reach a given layer thickness. Understanding jetting, spreading and final pattern shape formation during evaporation is key to controlling the practical applications of inkjet. We obtained interesting results in this direction through the study of silver nanoparticles printed lines. We could in particular show that the line width is independent on the nanoparticles’ concentration in the ink, and that line width and cross section area are predictable to the first level when extrapolating the values measured at small drop spacing. We also identified that the substrate thermal conductivity influences the final cross section profile through a variation in the evaporation duration. Further study of those key steps of the inkjet process is already considered.

Finally, we showed that the combination of the printing process and a subsequent electrodeposition step allows for a cost-effective fabrication of antennas on flexible substrates. We specifically applied this process flow to the implementation of RFID tags with demonstrated reading range above 5 m using a commercial RFID reader. Further developments are underway to put in practice this fabrication route for other electrical circuits on various substrates.

These developments will unfold in several important directions including the realization of printed devices, either passive, such as sensors, or active on a longer term, such as transistors and simple electronic circuits. All of these will retain the key advantages of being printable on various substrates, at low cost but with effective functionality.

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References

[1] Bidoki S M, Lewis D M, Clark M, Vakorov A, Millner P A and McGorman D 2007 J. Micromech. Microeng. 17 967
[2] Dasgupta S, Kruk R, Mechat N and Hahn H 2011 ACS Nano 5 9628
[3] Koo H-S, Chen M and Pan P-C 2006 Thin Solid Films 515 896
[4] Xua T, Gregorya C A, Molnara P, Cuia X, Jalotab S, Bhadurib Tran Nhan Ai, Tran Huy Nam, Dang Mau Chien and Dong H, Carra W W and Morris J F 2006 Adv. Nat. Sci.: Nanosci. Nanotechnol. 2 015014
[5] Tran Nhan Ai, Tran Huy Nam, Dang Mau Chien and Fribourg-Blanc Eric 2005 ChemPhysChem 6 1221
[6] Traminer J E, Smith P J and Derby B 2005 Mater. Res. Soc. Symp. Proc. 860E LL.2.6.15