Gas Sensor Devices Obtained by Ink-jet Printing of Polyaniline Suspensions

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Summary: We report on the fabrication process of a sensing device obtained by ink-jet printing of polyaniline suspension on alumina substrates. We optimized the inkjet parameters (amplitude and duration of jetting impulse, jetting frequency, substrate velocity) to obtain thin polyaniline lines as sensitive layers and we analyzed the morphology of PANI lines on substrate. Device response towards ammonia are also discussed and compared with reference device obtained by spin-coating.

Keywords: ammonia; ink-jet printing; polyaniline; sensor

Introduction

The ink-jet printing technique is an interesting and versatile method to make controlled deposition of functional materials with suitable geometry on various substrates.[1–4] It is low cost and does not need any temperature or vacuum processing. Furthermore it does not require any contact between the deposition system and the substrate. All these factors allow to choose the best substrate for the specific application. The only constraint of this technique is the requirement to have fluids with suitable viscosity (lower than 20cP) and surface tension (in the range 28–350 $mN \cdot m^{-1}$).[2]

In Drop on Demand (DoD) system, drops can be released as a consequence of piezoelectric actuation, obtained when electric pulse signal is active. Intensity and duration of pulse must be optimized for each ink to obtain stable drops in the volume range of 10 pL. Moreover to produce lines or films, the ink emission frequency and relative velocity between print head and substrate are set up to produce desired drop overlapping.

Recent studies have been evidenced that ink-jet printing of polymer is possible using dilute polymeric solution or suspensions.[2–4] Up to our knowledge, few works have published data relative to the application of ink-jet printing in the field of polymeric sensor devices.[4] In order to test advantage of ink-jet printing for film deposition, we have fabricated and characterized different ammonia sensing devices where the sensing layer has been obtained both by ink-jet deposition and spin coating (used as reference ammonia sensor). We optimized the inkjet parameters (amplitude and duration of jetting pulse, jetting frequency, substrate velocity) to obtain thin polyaniline (PANI) lines as sensitive layers. PANI is a conductive polymer[5] already tested as sensing material to realize ammonia sensor.[5–8] More generally, gas sensing properties of PANI depend on different factors (the nature of the dopant, the presence and the nature of substituents on aniline ring, etc)[6] among them the method of deposition.[6]

Experimental Part

Polyaniline (emeraldine salt) was purchased from Sigma–Aldrich. PANI chemical-physic parameters, submitted by Aldrich, are reported in Table 1. It was used as received.

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Table 1.
PANI characteristics (by Aldrich) and ink-jet parameters used to make sensing lines of this conductive polymer on alumina substrate.

Ink Characteristics	Ink-jet Parameters
Ink = Polyaniline (PANI)	**Nozzle diameter** = 70 μm
Concentration = 2–3 wt. % (dispersion in xylene)	**Voltage** = 50 Volt
Conductivity = 10–20 S/cm (film)	**Pulse length** = 80 μs
Viscosity = ∼3 cP	**Frequency** = 15 Hz
Density = 0.90–0.95 g/mL at 25 °C	**Substrate speed** = 750 mm/s
	Substrate = alumina (1 × 1.5 cm^2) with interdigitated Au contacts

Polyaniline (PANI) suspension was deposited on Al_2O_3 substrate (1.5 × 1 cm^2) with interdigitaded Au contacts. Two type of sensors devices were made with two methods of PANI deposition: spinning and ink-jet printing.

For ink-jet printing process we used a Microdrop MD-K-130-030 dispenser head. It was a drop-on-demand micro-head with a 70 μm diameter nozzle (corresponding to a drop diameter of about 80μm and drop volume of about 268 pL) driven by a piezoelectric device. Drops can be deposited with frequencies up to 2 kHz. A stroboscopic camera system provided visual control to adjust piezo-voltages and pulse durations for reliable droplet ejection and to avoid satellite drops.

The ink-jet parameters used to produce sensing devices based on three parallel PANI lines are reported in Table 1. Every PANI line was 7 mm long. In this experimental test alumina substrate was mounted on a sample stage with XY controlled movement, which had a resolution of 1 μm and an available workspace of 300 mm × 300 mm.

The PANI lines morphology was investigated by optical microscope (Polyvar MET Reichert-Jung), scanning electron microscope (LEO 1530) and surface profiler (Tencor P10).

To produce spinning film we deposited with glass pipette, drop by drop, ten drops of PANI on alumina spinning at 3000 rpm. These parameters have been optimized to produce a homogenous film with electrical resistance comparable with sample obtained by ink-jet printing (in the order of magnitude of 1 KΩ).

Sensing device response to ammonia has been measured using a Gas Sensor Characterization System (GSCS).[9]

Results and Discussion

In order to evaluate the influence of deposition technique on the final device response to ammonia, we have chosen alumina with gold contacts as a common substrate both for spin-coating and ink-jet printing depositions. This choice will not allow the film thickness analysis (presumably on the submicrometric range) due to the substrate roughness (in the micrometric range).

In Figure 1, it is reported the flow chart of logic and experimental steps followed to optimize ink-jet printing parameters to make sensor devices based on parallel lines of PANI deposited on alumina substrate with gold contacts.

In first step we have found control parameters for our piezoelectric system used in the microhead, to emit correctly the PANI fluid from the nozzle. Amplitude and duration of electric pulse must be found trying different values combinations. We used a trial and error procedure consisting of modifying parameters, following ink-jet printing theory and practical experience, up to make stable drops able to reabsorb all satellites produced at the beginning of the flight (Figure 2).

For our microhead nozzle (70 μm diameter) and PANI ink we found 50 V and 80 μs as suitable values respectively for pulse amplitude and duration (Figure 2 and Table 1).

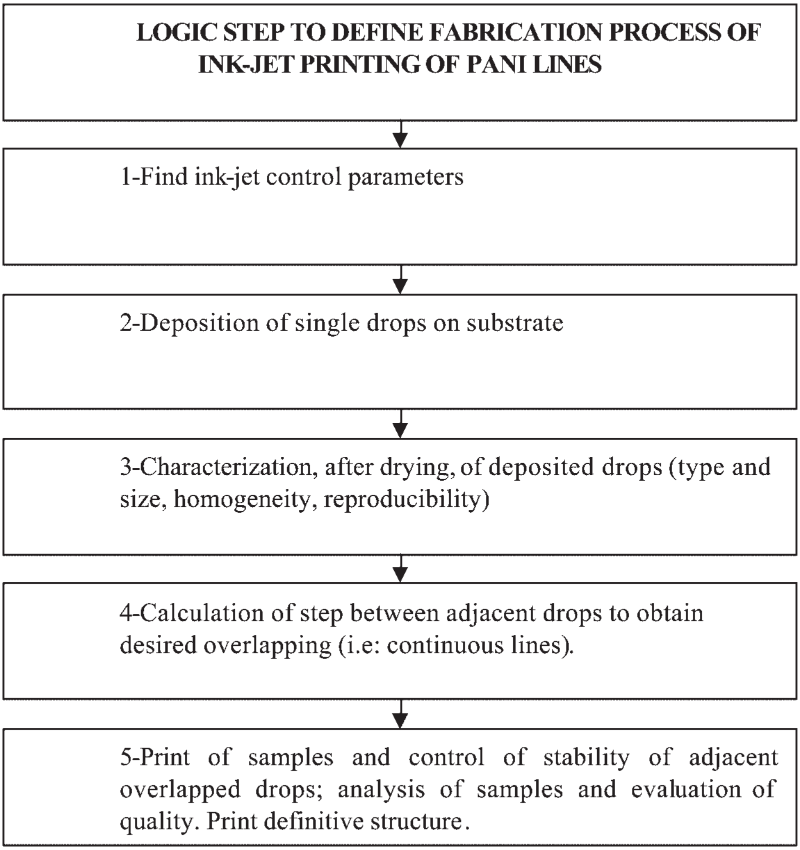

Figure 1.
Fabrication process of PANI line by ink-jet printing.

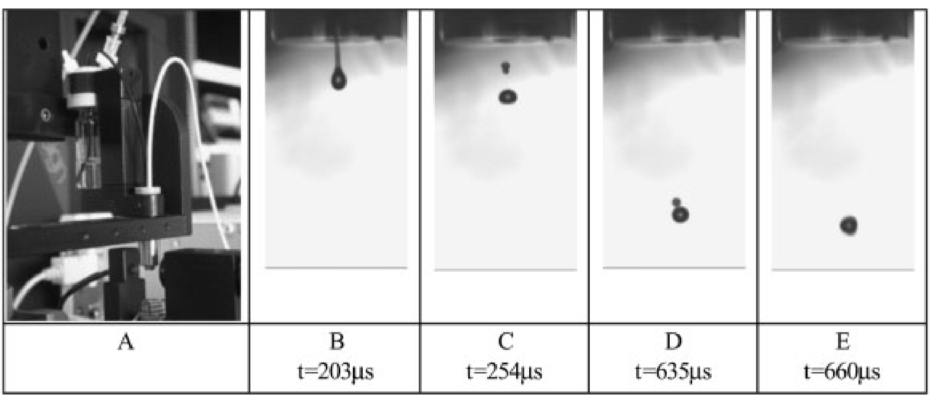

Figure 2.
Printer microhead (A) and image sequence taken during development and elongation of jet (B), break-up to form satellite drop (C), readsorbing phase of satellite (D) and fly of final PANI drop (E) made at 50V applied impulse. The images are obtained setting up stroboscopic videocamera with different delay times (reported below each photo).

In following experiments (2 and 3 of Figure 1) we deposited and characterized single drops on alumina. We wanted to verify the evenness of drop shape and to measure its diameter, thickness and profile. Optical microscopy analysis shows that a PANI drop on alumina is not a regular disc with an approximate diameter of 190 μm (Figure 3). The diameter of deposited drop is higher than that one of spherical emitted drop because this is spread on substrate due to alumina-PANI interaction. This influences also the sharp and thickness of final printed drop. Unfortunately thickness and profile is not available because alumina surface is too rough to accurately determinate the drop film thickness.

A line composed of adjacent stable drops can be adjusted in size and shape, acting on the partial overlap of drops on the substrate. When contribution of more drops is present in a point, deposited material will be thicker and wider than a single drop. The minimum width of a line is the drop diameter and the minimum thickness of a line is about the drop thickness.

Generally we use the equation (1) to calculate the percentage of overlapping (*%over*) between drops (step.4, Figure 1).

$$\%over = [(diam - step)/diam] * 100 \qquad (1)$$

where *diam* is approximate diameter of drop and *step* is the distance between centers of circular drops (see Figure 4).

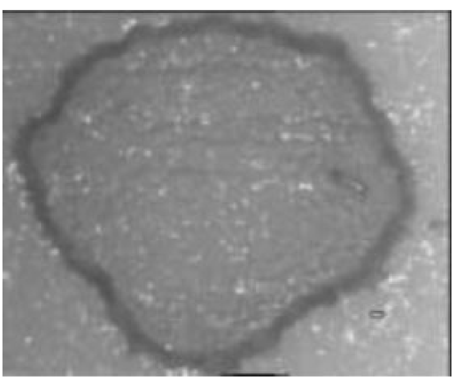

Figure 3.
Optical image of a single PANI drop deposited on alumina substrate.

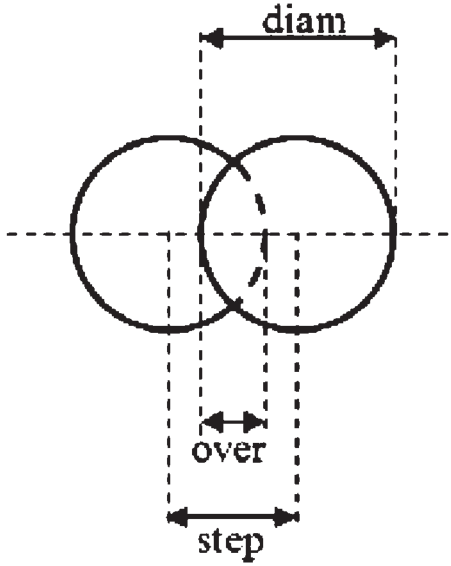

Figure 4.
Schematic representation of two overlapping circular drops.

To have a desired drop overlapping of a certain percentage the step between drops must be:

$$step = diam - [(\%over/100) * diam] \qquad (2)$$

After printing the drops, it is important to control the stability of adjacent-overlapped drops (step.5, Figure 1): in these experiments on alumina, drops partially overlapped remain undisturbed in their original landing position and they can be easily combined in continuous sequences to produce lines.

In Figure 5 we report different PANI test lines, printed on alumina, by changing velocity of substrate and emission frequency of PANI drops. The most regular shape (Figure 5D) has been obtained with drop frequency 15 Hz, substrate speed 750 μm/s, step between drops 50 μm, overlap about 73%. The width of these lines measured by optical microscopy are about 200 μm. It is comparable with the diameter of a single drop.

We used these parameters also to print on alumina substrate with Au contacts. In Figure 6 we show respectively the optical and SEM image of lines of PANI made on

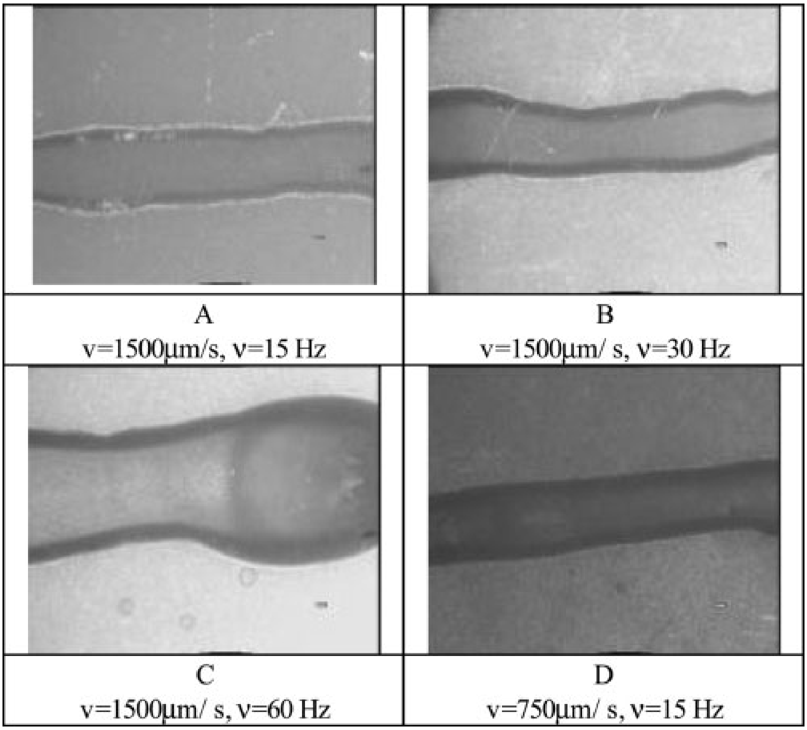

Figure 5.
Optical images (40×) of PANI lines printed on alumina substrate using different combination of substrate velocity and drops frequency.

this substrate. The part of fluid deposited on Au is at higher place respect to Al_2O_3, and tends to flow on Al_2O_3; this could explain the larger width of PANI lines, in the portion that is printed on Al_2O_3 between contacts in comparison with that ones present outside of Au contacts.

Gas Sensors

Sensor devices, obtained by inkjet printing (Figure 7B), have been tested in controlled atmosphere to measure electrical response of PANI to different ammonia concentrations. The results obtained with ink-jet type sensor have been compared in

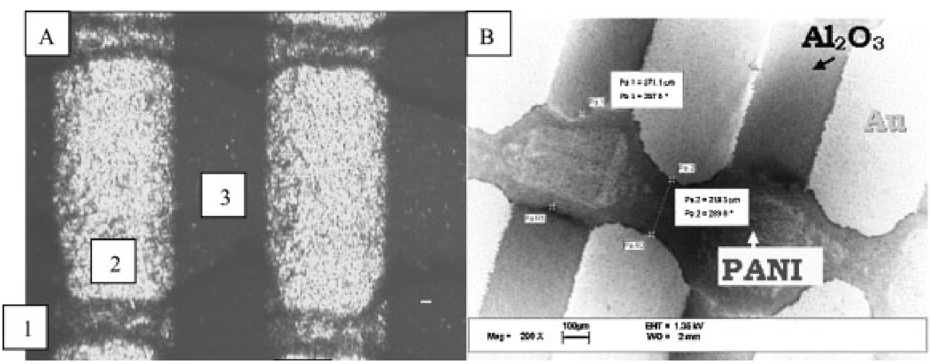

Figure 6.
Optical (A) and SEM images (B) of PANI lines (1) printed on Alumina (3) substrate with Au contacts (2).

Figure 7.
Images of final sensor devices made on Alumina substrate with Au contacts by spinning (A) and ink-jet printing (B) of a PANI suspension.

Figures 8 and 9 with that ones of spinning type sensor whose photo is showed in Figure 7A. The two sensor devices have been designed looking for comparable initial electrical resistance in order to evaluate the influence of deposition method.

We have chosen to carry on the measurements in presence of a fixed relative humidity being PANI a polymer sensitive to moisture. Figure 8 shows that both PANI spin film and ink-jet lines are sensitive to NH_3. The process is reversible but the recovery time is slow. As described in literature,[5–7] the resistance of sensor devices changes as a consequence of chemical interaction between PANI and NH_3.

The response to NH_3 of devices obtained by ink-jet is higher than the other one obtained by spin-coating (Figure 9). The difference between sensors is probably due to different PANI morphologies and response times. Other experiments are

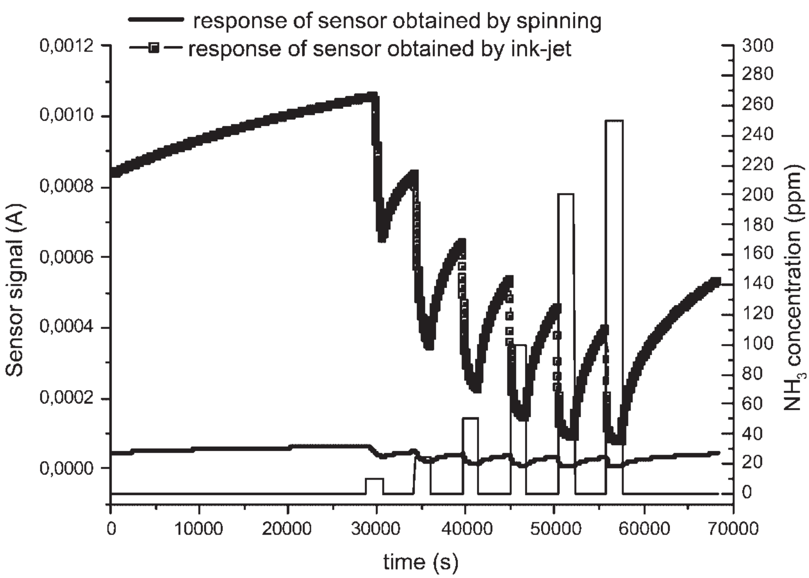

Figure 8.
Dynamic responses to ammonia gas of sensor devices obtained with different methods of PANI deposition. The response are obtained at 20 °C and 50% of relative humidity. The ammonia concentration in air is changed in the range 10–250 ppm.

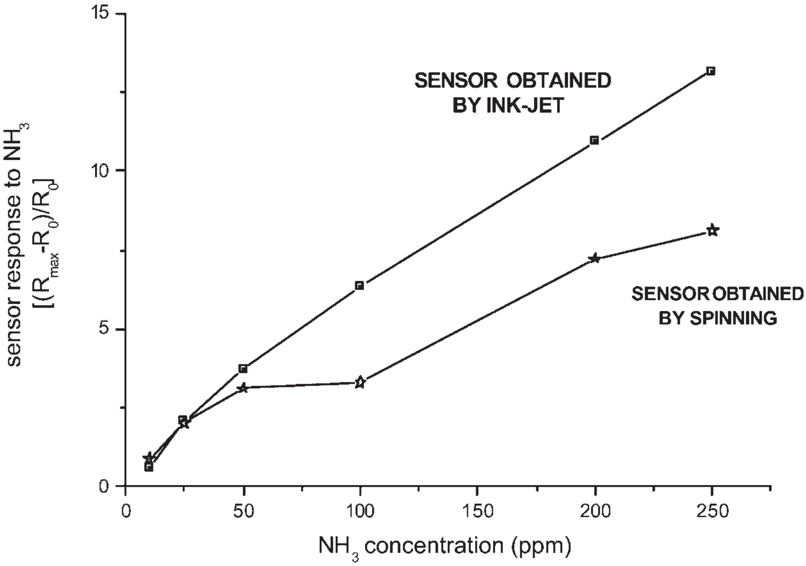

Figure 9.
Responses at different concentration of ammonia calculated, from dynamic curves of Figure 8, for sensor devices obtained with different methods of PANI deposition.

in progress, to better understand these differences between sensors and evaluate their stability.

Conclusions

We studied a procedure to optimize ink-jet parameters to obtain sensor devices based on polyaniline lines. This method of deposition allows to obtain in about 40 seconds a reproducible sensor device, using only 10^{-4} mL of a commercial PANI suspension.

A preliminary comparison between sensors obtained by ink-jet printing and spin-coating indicates that using ink-jet printing we can improve PANI sensor device characteristics.

The comparison between the responses to ammonia of reference sensor device obtained by spin-coating with that ones obtained by ink-jet shows that sensor response is clearly influenced by method of deposition, in particular reducing response times.

Acknowledgements: This work has been partially supported by the CAMPEC Project, funded by the Italian Ministry for University and Research.

[1] P. Calvert, *Chem. Mater.* **2001**, *13*, 3299.
[2] B.-J. de Gans, P. C. Duineveld, U. S. Schubert, *Adv. Mater.* **2004**, *16*, 204.
[3] E. Tekin, B.-J. de Gans, U. S. Schubert, *J. Mater. Chem.* **2004**, *14*, 2627.
[4] A. Bietsch, J. Zhang, M. Hegner, H. P. Lang, C. Gerber, *Nanotechnology* **2004**, *15*, 873.
[5] N. E. Agbor, M. C. Petty, A. P. Monkman, *Sens. Actuators B* **1995**, *28*, 173–179.
[6] D. Nicolas-Debarnot, F. Poncin-Epaillard, *Analyt. Chim. Acta* **2003**, *475*, 1.
[7] A. L. Kukla, Y. M. Hirshov, S. A. Piletsky, *Sens. Actuators B* **1996**, *37*, 135.
[8] V. V. Chabukswar, S. Pethkar, A. A. Athawale, *Sens. Actuators B* **2001**, *77*, 657.
[9] L. Quercia, F. Loffredo, B. Alfano, V. La Ferrara, G. Di Francia, *Sensors and Actuators B* **2004**, *100*, 22.