Inkjet Printing of Chemiresistive Sensors for the Detection of Volatile Organic Compounds

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Abstract

We report about inkjet printing of chemiresistive sensors for the detection of volatile organic compounds (VOCs). The sensor comprises three fully inkjet-printed layers of (i) silver interdigitated electrodes (IDE), (ii) multi-walled carbon nanotubes (MWCNTs) and (iii) poly (styrene-co-maleic acid) partial isobutyl/methyl mixed ester (PSE) deposited on glass and polymer substrates. A composite-like structure of PSE and MWCNTs could be obtained by applying optimized printing parameters. Thus, this layer can act as chemiresistive vapor sensor due to the change of electrical resistance in presence of selected VOCs. We have studied the response of the sensors to various VOCs and different vapor concentrations of the VOCs. To investigate the morphology and the properties of the inkjet-printed thin films, profilometry and scanning electron microscopy (SEM) as well as electrical measurements were employed.

Introduction

Today organic chemical liquids and vapors are widely used in various fields of industry and daily life. Especially the vapors can present serious medical dangers due to inhalation by humans or absorbance through the skin next to general environmental and explosive dangers [1]. Therefore, possible applications of VOCs sensors range from monitoring fuel tanks, air pollution in cities or industrial plants to sensors for medical applications, food quality and odorless chemicals (e.g. drugs).

In literature, several types of sensors for VOCs are described such as metal oxide semiconductor sensors, surface acoustic wave sensors, quartz microbalance sensors, chemiresistive or chemicapacitive sensors and others [2-6]. In particular chemiresistive sensors offer several advantages in terms of simplicity and flexibility. Compared to other sensors for the detection of VOCs, chemiresistive sensors do not require heating, mechanical excitation, light sources, sophisticated power sources and circuits or other complex surrounding accessories [1, 7]. Therefore, they are considered as a promising platform for low-power, low-maintenance, compact and flexible sensor devices [7].

Chemiresistive sensors can be divided in two main types. They can be based on (i) polymer materials that are conductive because of their electronic structure or (ii) composite materials of conductive particles such as metal or carbon distributed in an insulating polymer matrix. Common to these different types of VOCs sensors is their functional principle that is based on vapor sorption by sorbent polymers. Due to the vapor sorption a swelling process of the polymer is initiated increasing the resistance of the composite [8]. Thus, the sensors allow a simple direct-current resistance measurement [7]. The sorbent polymers play a key role for the sensor devices as the degree of swelling strongly depends on the type of polymer and the VOC. The chemical selectivity of the sensor depends on the structure of the polymer and can be easily changed through polymer synthesis or by choosing other polymers.

In last decades the application of carbon nanotubes (CNT) as conductive material in composite layers have been reported intensively [9-17]. CNT/polymer composite sensors offer high sensitivity, fast response and long-term stability [9]. However, the efficient and low-cost manufacturing of CNT/polymer based chemiresistive sensors is a current challenge towards industrialization.

Here, we focus on a simple and reliable preparation of the sensors using inkjet printing technology. The sensors we present can be printed on flexible substrates such as PEN enabling a roll-to-roll processing.

Experimental

Sensor Design

The chemiresistive sensor consists of electrodes and the sensing materials printed layer by layer on top of each other. Cleaned glass slides and PEN were used as substrates (cleaning was carried out with ethanol and deionized water to remove organic residuals followed by a high pressure air flow to dry the substrate). Figure 1 shows the architecture of the sensor. As the first layer, interdigitated electrodes (IDE) were deposited. With the help of the electrodes the resistance change during exposure to VOCs can be monitored. Finger width and finger separation distance were set to 200 μm. The size of the pattern is about (3 x 3) mm. The second layer is the sensing layer based on a composite of polymer/CNTs. In general, the composite can be prepared by either deposition of (i) blended CNTs and polymers or deposition of (ii) separate layers of CNTs and polymers (sequential deposition). The blend can yield a complete composite film while the separately deposited materials generate a composite-like layer at the interface of both materials. We performed the latter preparation method by sequential inkjet printing of two separate layers of CNTs and polymer in order to avoid the challenges concerning the development of a well-dispersed ink formulation of CNTs and polymers.

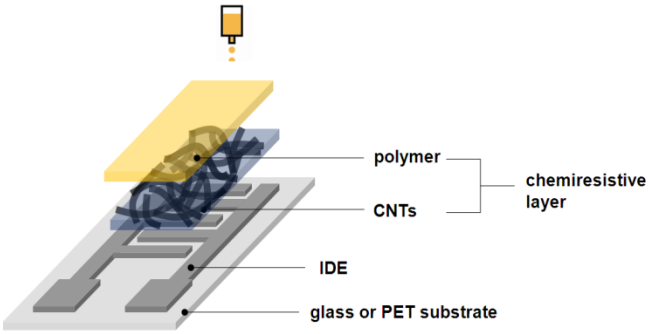

Figure 1. *Design of the fully inkjet-printed sensor*

Materials

SunTronic SunJet Silver EMD5603 obtained from Sun Chemical was employed to create the IDE patterns.

An ink formulation based on MWCNTs was prepared by adding 0.2 wt% MWCNTs into an aqueous solution of 0.5 wt% sodium dodecyl sulfate (SDS). SDS acts as surfactant to stabilize the MWCNTs in water. The MWCNTs were purchased from Southwest Nanotechnologies and have an outside diameter between 10 and 30 nm and a length of about 1 to 2 µm. To disperse and unbundle the MWCNTs, high frequency pulses of the ultrasonic homogenizer (Bandelin, model HD 3200) were applied for 15 min before intense centrifugation for 20 min at 20,000 rpm for separating the remaining large or agglomerated particles. Due to the ultrasonic and centrifugation treatment the length of the MWCNT was decreased to < 1.2 µm. Finally, the upper part of the dispersion was extracted and filtered with 5 µm pore-sized disposable syringe filter prior to printing.

Poly (styrene-co-maleic acid) partial isobutyl/methyl mixed ester (PSE) powder (purchased from Sigma Aldrich) with average molecular weight Mv of about 180,000 was applied as polymer responsible for the chemical sorption of the VOCs. In previous work the sensitivity of the polymer was investigated using different VOCs [13]. It turned out that the highest response of the polymer was obtained by exposure to ammonia and amine compounds. 0.5 wt% of the PSE powder was dissolved in acetone by applying a magnetic stirrer for 10 min. To remove remaining particles, the mixture was filtered using 5 µm pore-sized disposable syringe filters prior to inkjet printing.

Ammonium hydroxide, ethanol, acetone, triethylamine and tetrahydrofuran were used as analyte for the sensor tests in vapor concentrations of 50, 200 and 500 ppm.

Inkjet printing

Inkjet printing of the silver IDE was carried out on a Dimatix Materials Printer 2831 (DMP, printhead with 10 pL nominal drop volume). The jetting conditions were adjusted until a stable drop formation was obtained. The resolution was set as 1016 dpi. During the inkjet printing process, the substrates were heated to 55 °C to improve the line morphology of the silver IDE. Subsequently, the deposited silver layer was sintered at 150 °C for 5 to 10 min on a heating plate in ambient condition.

The water-based MWCNT ink formulation as well as the PSE dissolved in acetone were printed on top of the sintered electrodes using an Autodrop single nozzle dispensing system from Microdrop Technologies (69 µm nozzle inner diameter). Drop distance and printing speed were set to 100 µm and 2 mm/s, respectively. The substrate temperature was set to 75 °C during printing to improve the evaporation of water and the assembly of the MWCNTs. Drop distance and printing speed for the PSE formulation were maintained to 100 µm and 10 mm/s, respectively. Finally, the fully inkjet-printed sensor was heated to 150 °C for about 10 min to remove remaining solvents and impurities.

Characterization

The responses of the sensors to the vapors of the VOCs were investigated under a static system (closed chamber) at room temperature. Therefore, single VOCs were injected into the chamber and the resistance of the printed sensor was monitored in-situ during the exposure to the VOCs. To obtain the sensor response, the resistance of the sensor was determined in two periods. The first period was limited to 2 min and is defined as reference resistance R_0 without exposure to any VOCs. In the second period, a single VOC was injected into the closed chamber and the output signal R_{VOC} was recorded for maximum 7 min to obtain a steady-state condition as result of a saturation limit.

To determine average thickness and average surface roughness of the printed layers profilometry scans were performed (Dektak 150, Veeco Instruments). Sheet resistance was investigated by four point probes arranged in a square of about (3 x 3) mm according to the method of van der Pauw.

Results and Discussion

In the first attempt all the materials are individually deposited on glass substrates to determine the layer morphology and sheet resistance. A summary of the measurements is shown in Table 1.

Table 1. Average thickness, average roughness and sheet resistance of printed layers on glass substrate

Inkjet-printed films	Average thickness (nm)	Average surface roughness (nm)	Sheet resistance (Ω/□)
SIDE	222 ± 13	62 ±10	6.3E+00 ± 5.0E-01
Individual MWCNTs	195 ± 19	240 ± 3	2.2E+06 ± 1.7E+03
Individual PSE	164 ± 14	40 ± 3	1.8E+08 ± 3.1E+05
MWCNTs/PSE	385 ± 46	138 ± 2	2.7E+06 ± 1.4E+03

As indicated in Table 1, the printed MWCNT film exhibits a remarkable high surface roughness. This is caused by an inhomogeneous distribution of MWCNTs. Figure 2 proves the inhomogeneous distribution as there are clearly evident line-shaped features. This line formation can be explained in terms of evaporation-induced flows inside the inkjet-deposited droplets [18]. However, the rough surface of MWCNTs layer benefits the formation of an interfacial layer by adding the PSE polymer on top of the MWCNT layer. A comparison of the sheet resistance values for the individual MWCNTs and the MWCNTs covered with PSE reveal an increase of sheet resistance indicating a strong penetration of the insulating polymer into the CNT network.

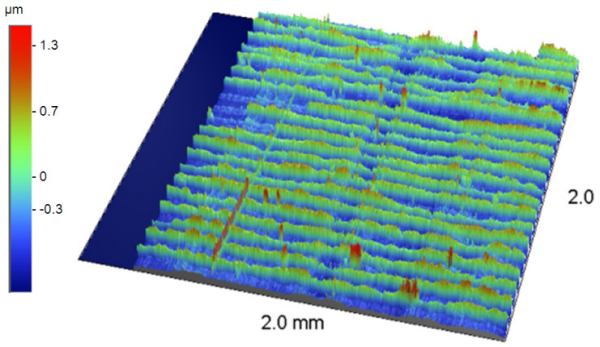

Figure 2. *3D map scan of a thin film of MWCNTs printed on glass substrate*

To investigate the microstructure of the printed MWCNT/polymer layer a top-view was obtained using scanning electron microscopy. According to figure 3, the CNTs are embedded in the insulating polymer which is an evidence that a composite-like layer morphology can be generated by sequential inkjet printing of CNTs and polymer.

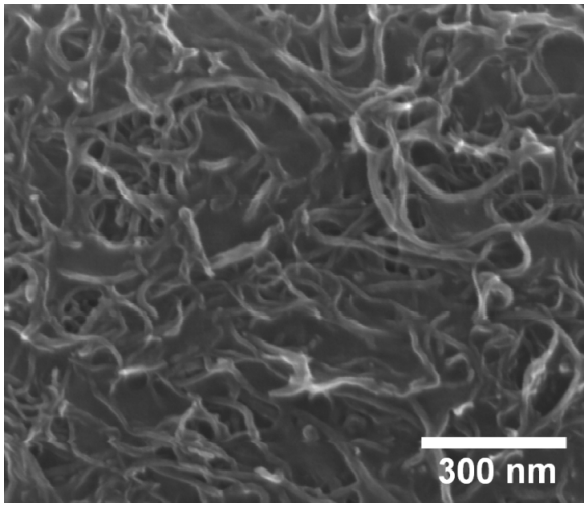

Figure 3. *Composite-like structure of MWCNTs and PSE*

Figure 4 represents the functional principle of the inkjet-printed chemiresistive sensor. The transduction mechanism of the sensor can be described on the basis of percolation theory. PSE has the property to collect and concentrate VOC molecules by reversible sorption. Specific chemical properties and further

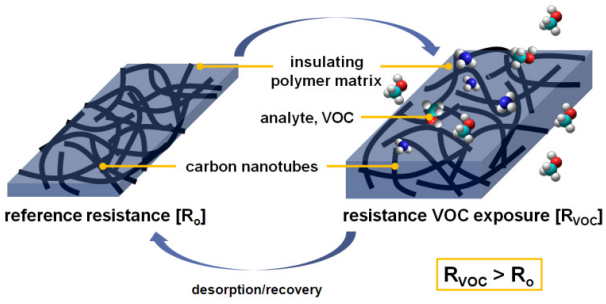

Figure 4. *Functional sensing principle of chemiresistive layers*

parameters that affect the sorption of the molecules are described on the basis of Hansen solubility parameters or linear salvation energy relationship elsewhere [19, 20]. Due to the chemical sorption a physical swelling process of the polymer is initiated resulting in a change of the conductive pathway of the composite film and thus to an increase of resistance.

Figure 5 shows the results of the sensor response after injection of different single VOCs. According to the theory of chemiresistive sensors they exhibit an increase of resistance when the sensor was exposed to the VOCs. As a result, the sensor shows the highest response for all concentrations to ammonium hydroxide as it was proven in previous works [13]. The electrical responses to other VOCs were ranked as triethylamine, ethanol > acetone > tetrahydrofuran. Obviously, a nonlinear response can be found when the sensors were tested with varying amounts of VOCs.

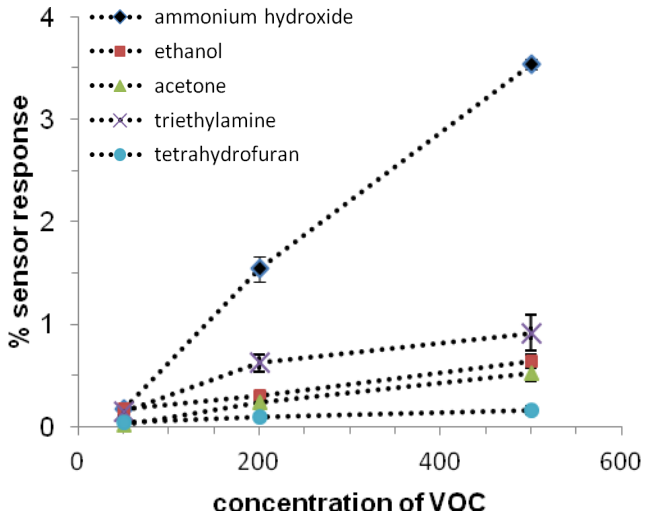

Figure 5. *Sensor response of the fully inkjet-printed sensors as function of different VOCs and concentration of VOCs (connection lines between the measurement points are lines to guide the eyes)*

Conclusion

A fully inkjet-printed chemiresistive sensor was demonstrated based on silver IDE and separately printed MWCNTs and PSE. The insulating PSE can be incorporated using inkjet printing into the MWCNT network by taking advantage of the high roughness of the CNT film. The results indicate a good contact of MWCNT/PSE and MWCNT/MWCNT yielding a composite-like film formation qualified for chemiresistive sensor applications. The resistance change was measured in-situ during exposure to the analyte using the printed silver IDE. The MWCNT/PSE sensor exhibits a high selective response to the vapor of ammonium hydroxide. Our sensors can operate at ambient conditions and do not require light or heating sources.

Inkjet printing turned out as promising manufacturing method for low-cost, compact and flexible chemiresistive sensors which can be considered as an important step towards industrial applications. As the sensor can be manufactured on flexible substrates such as PEN, a roll-to-roll process is possible to scale up the production.

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Enrico Sowade received his Master of Arts (M.A.) in print and media technologies from Chemnitz University of Technology in 2009. Since then, he has been working at the Department of Digital Printing and Imaging Technology (Chemnitz University of Technology). His research primarily focuses on self-assembly processes in inkjet printing. Enrico Sowade is a member of the Materials Research Society (MRS).