Printing Sensor on Flexible Substrates for Detection of Volatile Organic Compounds

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***Abstract*—This paper investigates printing functional materials on diverse flexible substrates for rapid detection of volatile organic compounds (VOCs). Inkjet printing and doctor blade coating is performed for rapid manufacturing of the sensing devices. The three different substrates selected are polyethylene terephthalate (PET), cotton fabric and a common A4 type printing paper. The structural and morphological properties of the substrates are exploited to compare the detection of three different types of VOCs, such as acetone, ethanol and isopropanol. A silver (Ag) nanoparticles-based ink at suitable properties for inkjet printer is used for developing the interdigital electrodes. A nanocomposite of Carbon-based paste is applied as sensing layer. Geometrical parameters of the devices, materials, processing and sintering conditions are kept similar, to only explore the distinguished sensing capabilities based on the substrate materials. Two different concentrations i.e. 4 and 22 ppm (parts per million) of the representative VOCs are applied in the test chamber and corresponding chemoresistance values are recorded using a sourcemeter. The different resistance peak values and responses times are correlated with the type of substrates and a comparative study is performed based on the type of substrate. This research presents greater contribution in the field of large area, cost-effective and wearable VOCs sensors that are highly demanding both for industrial as well as environmental monitoring. Some of these VOCs are considered as potential bioanalytes, which can be used in the recognition of several chronic diseases using these wearable sensing devices.**

Keywords—Printed Sensors, VOCs, Inkjet Printing, Coating, Thin Films

I. INTRODUCTION

Printing sensors and electronic devices on diverse polymeric substrates have attracted significant interest in recent years, with a focus on developing cost-effective manufacturing techniques along with easy processing of a wide range of materials [1, 2]. The development of electronic components on unconventional substrates such as plastics, paper and textiles offer unique properties such as mechanical flexibility, lightweight, conformability and in some cases biocompatibility and biodegradability. These interesting properties of substrates make them distinguished in most cases from standard silicon-based devices, where the above-stated traits are of main concern [1-3]. The solution-based printing approach is preferred on the polymer substrates for their incapability to withstand higher temperatures as well to reactive chemicals involved in the clean room micro-manufacturing processes. The whole printing process is completed in few steps, where a colloidal solution is patterned directly on the target substrate. The location specific deposition reduces the materials' wastage and thus making the printing process unique and advantageous for cost-effective manufacturing [4]. The recent developments have resulted already in various proof of concept devices, which have a laid an effective platform for the future flexible, foldable and stretchable electronics at larger scale [5]. Among the different developed devices, printed gas sensors on polymeric substrates are particularly explored for their extensive use in industrial and environmental monitoring of volatile organic compounds (VOCs) as well as toxic gases [6].

Conventionally gas sensors are developed through standard micromachining and photolithography techniques in clean room processes, while utilizing rigid substrates particularly thin membranes and using metal oxides (MOX) as sensing layers [7]. The large number of steps including masking, membrane etching for reducing thermal budget and multilayer structures make the manufacturing costly and restricted to the developers having access to these sophisticated tools [8]. Therefore, the recent developments in printing technologies and engineered nanomaterials have opened new avenues for developing gas sensors on diverse substrates and at much affordable manufacturing costs. MOX based sensors have been reported with better performances in terms of sensitivity, selectivity and robustness etc., however their high temperature processing during the manufacturing for annealing the MOX layer make them restricted to a certain class of substrates having higher glass transition (Tg) temperatures [9]. This higher Tg make it more challenging to develop MOX based gas sensors on polymeric substrates, which have lower Tg i.e. <150 ^{o}C. Therefore, the recent advancements in low temperature processing nanomaterials have provided alternative solutions to embed gas sensing layers in a simple fashion on versatile substrates. Among the newly developed nanomaterials, carbon-based nanocomposites have produced promising results and have been successfully applied for a wide range of gas sensing applications [10].

The low cost, simple processing, synthesis of stable printable solutions with rheological properties ideal for the specific type of printing technology, make carbon a distinguished candidate among the available printable materials. Carbon based nanocomposites have been investigated widely at different mixing ratios with compliant solvents and surfactants targeting a variety of applications such as electrodes, interconnects as well as sensing layers in different printed physical and electrochemical sensors. Inkjet printing and doctor blade coating are the most feasible and easily accessible printing techniques among the list of available additive manufacturing processes. Therefore, these two techniques have been adopted in this research for development of VOC sensor on different polymeric substrates. Silver (Ag) nanoparticles-based ink is used with inkjet printing for developing the conducting electrodes and interconnects, whereas carbon-based nanocomposite is deposited using doctor blade technique. A comparative study based on the printability, robustness, bendability and finally the role of carrier substrate on the performance of sensors against different VOCs is performed. Different mixing ratios of the carbon nanocomposites are synthesized, and printability evaluated with a focus on layer thicknesses and physical adherence to the target substrate. Three different substrates including paper, polyethylene terephthalate (PET)

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and cotton-based fabric are utilized for developing VOC sensors. The porosity of the two substrates i.e. paper and cotton fabric play significant role in adsorption and desorption of the VOC molecules and therefore, have a direct influence on the sensitivity and response time of the sensors. These sensors are intended for development of wearable gadgets to monitor VOCs in the surrounding environment as well as biomarkers for different chronic diseases.

II. Materials

A. Substrates

Substrates are the basis for establishing a feasible fabrication route and play significant role in the design of experiments especially for using printing technologies. The glass transition temperature (Tg) of substrates is the main deciding factor for selection of dissimilar materials in multilayered devices and thus guarantee the perfect match at the interfaces as well as in the bulk of deposited films. Thermal budget of the whole process is bound to the Tg of substrate; therefore, selection of the substrates predominantly specifies the higher limit of the thermal treatments required for different materials during the printing processes. Besides the Tg, another important parameter is the chemical inertness of these substrates to the different chemicals added as solvents and surfactants to the colloidal solutions. A combination of a set of different thermal, mechanical and chemical attributes of the substrates is essential to any of the adopted printing technique. Keeping in mind these parameters, we selected PET, paper and cotton fabric substrates and were tested at desired thermal conditions before depositing the solutions. The substrates were tested at elevated temperatures as high as 150 ^{o}C, which is the highest value to reach for the intended materials to be printed on. No degradation in the substrates were observed during these thermal tests by observing the texture under an optical microscope as shown in Fig. 1. Also, the pore sized checked under the microscope for the paper and cotton substrates are about 2 and 5 µm respectively, which are ideal for enhanced adsorption and desorption of the VOC molecules. Besides the robust physical properties of these substrates, the light weight and conformability of these substrates make them ideal candidates for wearable electronic and sensing applications.

B. Electrodes and Sensing Materials

Printing of uniform conductive structures is the foremost priority and backbone of electronic devices either as constituent layers of a device or interconnect lines. Silver (Ag) is the most frequently reported printable conductor due its abundant availability at lower cost and capability of synthesizing stable solution with longer shelf life. The interdigital electrodes (IDEs) were printed using silver (Ag) nanoparticle solution. Ag ink especially developed for inkjet printing was purchased from Sigma Aldrich (product no 901971) and used without any further modifications. The Ag nanoparticles loading of ~38% in ethylene glycol is at the right viscosity range i.e. ~10 cP required for drop on demand inkjet printing system.

A nanocomposite of carbon black was developed for the sensing layer. Carbon ink purchased from Sigma Aldrich (product no 699624) and mixed in ethylene glycol at ~20 wt.%. Different mixing ratios were tried at first and

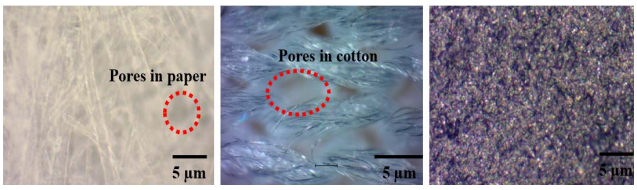

Fig. 1. Substrates, (a). PET, (b). Paper, (3). Cotton Fabric

printability of the solution was tested on the target substrates. Concentrations less than 20 wt.% showed printing with more nonuniform edges due to the rapid flowability and thinner layers resulting into highly resistive films. Concentration higher than 20 wt.% were more resistant to print a uniform layer and were more conductive, which was beyond the desired conductivity ranges. The synthesized solution with 20 wt.% has a viscosity of ~22 cP, which is in the suitable range for doctor blade coatings.

III. Printing Experiments

Proper cleaning of the substrates and surface activation are the preliminary steps, that influence the quality of the printed patterns on polymeric substrates. Therefore, the substrates were cleaned by following a standard protocol. PET substrate was subjected to wet cleaning approach where, it was immersed in isopropanol for 5 minutes followed by 5 minutes rinsing in deionized water. Substrate was dried using dry air and another dehydration step of keeping in an oven at 100 ^{o}C for 10 minutes was followed. Surface activation was done with the UV ozone cleaning system (Osilla). The system is operated at constant current and output intensity; therefore, a time-based activation was evaluated for optimization of this step. The optimal time deduced from this cleaning cycle as approximately 3 minutes, which gave best printing results. Rest of the two substrates i.e. paper and cotton fabric were dusted off by using pressurized air and the dehydration step of keeping in oven at 100 ^{o}C was executed.

The drop on demand inkjet system i.e. Dimatix (DMP 2850) was used for patterning the electrodes and interconnect lines, whereas doctor blade coating was adopted for sensing layer deposition. The nanoparticle suspension in the viscosity ranges of 10-12 cp is ideal for jetting micrometers sized droplets at specific frequency and voltage peaks. The piezoelectric transducer embedded in the inkjet nozzle head activates the microdroplets jetting and are placed on the target substrate in such a way that connected/overlapped droplets result into a patterned structure. Volume of the droplets is partly dependent on the rheological properties such as viscosity, surface tension, average particle size and vaporization points of the surfactants. Process related control parameters that have a direct bearing on the volume and speed of the droplet generation include the piezoelectric actuation controlled by pulsating waveforms, voltages, jetting frequencies, meniscus set-point, orifice size of the nozzle and the stand-off distance of printhead from the target substrate. The droplet spacing is an important process parameter which is directly corelated with the surface properties and is adjusted accordingly, to obtain regular and uniform sized patterns. All these parameters were adjusted for the Ag ink to print the interdigital electrodes (IDEs), interconnects and pads on all the three substrates. Fig. 2 (a

and b) show schematic diagrams of the inkjet printing mechanism and the sensor structure respectively.

A. *Printing Electrodes*

IDEs were deigned and printed in a way to cover the effective area suitable for the VOC sensing. Therefore, IDEs of different widths and lengths were printed using Ag ink. The length and spacing across electrode fingers were experimentally validated and the most suitable design with the desired effective area of 3×3 mm^2 was selected. The IDEs consisted of 3 fingers each with a width of 200 µm and spacing kept at approximately 800 µm as shown in Fig. (2(a&b)). The nozzle printhead with 10 pL size was used to print the Ag electrodes. For surface activation, UV ozone treatment of the PET substrate was performed for 3 minutes. This value was also optimized experimentally by cross checking the print quality against the exposure time to UV. Rest of the two substrates were not subjected to UV activation and were used directly for printing. The printing parameters such as jetting waveform, drop velocity (7mm/sec), stage temperature (45 ºC), frequency of 2 kHz, stand-off at 500 µm and droplet spacing at 25 µm were selected in the Dimatix drop manager software. Total of three printing cycles following wet on dry deposition were executed at a 1-minute interlayer delay. The printed structures were sintered in oven at 140 ºC, for 1 hour as recommended by the ink supplier.

B. *Printing Sensing Layer*

Doctor blade technique was used for deposition of carbon-based sensing layer. The as printed Ag electrodes were taken out of the furnace and put on the stage prepared for the doctor blade coating. Electrodes on PET substrate were treated again with UV ozone, whereas rest of the two substrates i.e. paper and cotton fabric were used without doing treatment. A shadow mask with the desired deposition area was prepared using a laser cutter tool. A rectangular mask with 3×3 mm2 was used to cover the respective area within the Ag electrodes shown in Fig. (2 (b)). The shadow mask thickness defines the layer thickness to be deposited and a sheet of about 80 µm was used to meet the desired thickness i.e. ~50 µm after sintering. A hotplate was utilized to pre-heat the substrate at 60 ºC, which helps in rapid evaporation of the surfactants while depositing. Two printing cycles following forward and back-printing approach was performed with an inter layer delay of 10 minutes. The pre-heating worked as a partial curing step of the deposited layer and a final hard bake was performed in at 130 ºC for 1 hour.

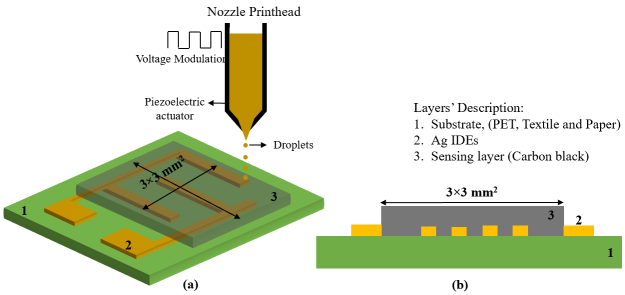

Fig. 2. Schematic of the printing and geometric parameters of the sensing device, (a) Schematic of inkjet printing and top view of the device, (b). Cross-sectional view of the sensing device

IV. Results and Discussions

A. *Physical and Electrical Characterizations*

Quality of the printed films determine the optimal physical and electrical properties, and therefore need proper consideration. Ag IDE patterns i.e. 200 µm wide with gaps in between 800 µm with high accuracy were printed repeatedly without any noticeable variations. An accuracy of ±5 µm was achieved by repeatedly printing the similar structures on all the three substrates several times and the overall effective area remained in close proximities. The multiple printing cycles lead to higher aspect ratios of the printed films as well as the increasing width of the printed lines with irregular edges. These issues are critical for plastic substrates such as PET, but the absorption capability of the paper and cotton fabric substrates do not experience such behavior. The impregnation of these deposited materials allow dissolution inside the bulk of substrate and hence become an intrinsic part of it. This improves strongly the adhesion of dissimilar materials to the target substrates. The porosity of paper and cotton fabric substrates allow the penetration of solution-based materials, which have minimal impacts when devices developed on top of these substrate are subjected to bending or mounting on nonplanar structures. Thickness of the printed lines is measured using a mechanical profilometer. The absorption and ultimate impregnation of the ink with paper and cotton fabric substrates make it difficult to discriminate between the printed layers and substrate surfaces, therefore the thickness results were relied only on the PET substrate. Thickness of about 1 µm was achieved as shown in the graphs in Fig. 3 (a). A slight variation in thickness is observed as can be seen from the profiles of Fig 3 (a) due to the spreading out of the ink onto the boundaries with more number of printing cycles. However, it did not affect the performance of the final fabricated devices. Fig. 3 (b) shows thickness profile of the coated carbon sensing layer. A thick layer of approximately 2 µm is achieved from a single coating step. The results shown are also taken from PET substrate, as the carbon layer merges with cotton fabric and paper substrates. Adhesion loss test was performed using scotch blue tape on all the three substrates after printing the Ag and the carbon layer afterwards. No delamination of the structures in both

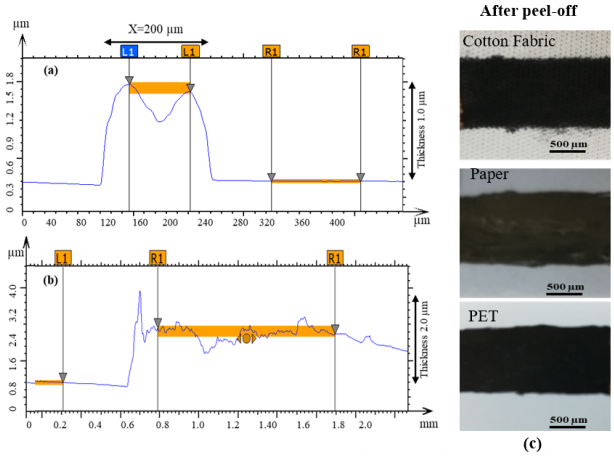

Fig. 3. (a) Thickness measuremenst of the Ag, (b) carbon films, (c) adhesion loss test after peeling-off

the printed layers were observed as shown in the Fig. 3(c). Electrical conductance of the printed electrode was achieved in the desired resistivity value at around 20 μΩ-cm after sintering in the oven.

B. Testing Setup

A lab-made testing chamber was developed to generate respective concentrations of the intended VOCs. The sensors were placed in an airtight test chamber with two openings at the ends, one for air injection and another for evacuation. An air-gun was used for priming the test chamber as well as ventilating after gas injections. Lead wires connected to the pads were linked to the sourcemeter (Keithley 2450) for data measurements. Three different volatile organic analytes i.e. acetone, ethanol and isopropanol were tested with the fabricated devices. Two different quantities i.e. 5 μl and 25 μl were selected for these tests. Geometric parameters and injected quantities of the VOCs were adjusted and calculated to generate concentrations of approximately 4 and 22 ppm. A voltage pulse of 2V at a time interval of 0.5 seconds was applied and resistance recorded with QuickIV4.1 software. Desired amount of the VOC was dropped into the chamber with the help of precise micropipette at the end of stabilization step of the sensor. Airflow for at least 3 seconds was blown to equally distribute the vapors inside the chamber and sealed the inlet with the gum. Both the inlets remained closed until the sensors response reached the saturation value. Similar testing protocol was repeated for all the three analytes.

C. Sensing Results

Change in the base resistance of the sensing layer is evaluated as a detection level for the corresponding VOC. The baseline resistance achieved after stabilization cycle is used as reference, which increases upon exposure to the analyte vapors. The two concentrations were selected to find the trend of the sensing devices and find the minimum level of detection. Fig. 4, 5 and 6 (a and b) show graphs of the sensors' response as a change in resistance for 4 and 22 ppm for PET, paper and Textile substrates respectively. Sensors' response is studied and compared based on the type of analyte and the type of substrates. Fig. (4-6) show influence of the substrate predominantly on the base resistance, although the printing parameters were kept similar for all the substrates. The change in resistance is due to the change in texture and composition of all the three substrates. Base resistance on the PET substrate is higher compared to paper due to the spreading out of the ink unevenly as a result of multiple printing cycles. PET substrate does not absorb partially the solution due to its plastic composition and therefore, cannot contain the sensing materials at the desired peripheries. Despite the higher base resistance recorded with sensors on PET substrate, higher cumulative resistance change was recorded. Higher sensitivities were recorded with the sensors on PET substrates as well. Comparable results are observed with the other two substrates, which produced sensitivities in close ranges at both the concentrations of the three analytes. Response time and restoration to the baseline resistance values are observed to be in the close ranges except for the sensors on PET substrates. A rise time of approximately 1.5 minutes is recorded for above 60% of the cumulative resistance change for the PET substrate, whereas the response time for sensors on paper and cotton fabric substrates lies within 1 minute. Similarly, a contrasting behavior for the fall time is also observed, where the sensors

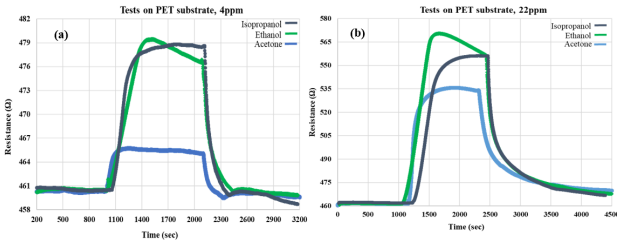

Fig. 4 (a) Sensing results on PET substrate at 4 ppm, (b) 22 ppm

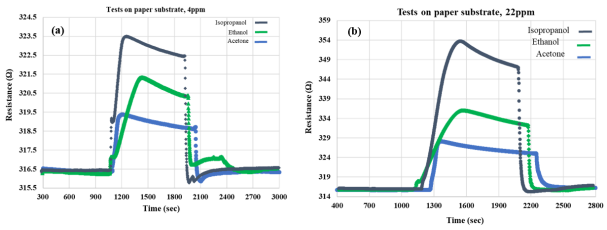

Fig. 5 (a) Sensing results on paper substrate at 4ppm, (b). 22 ppm

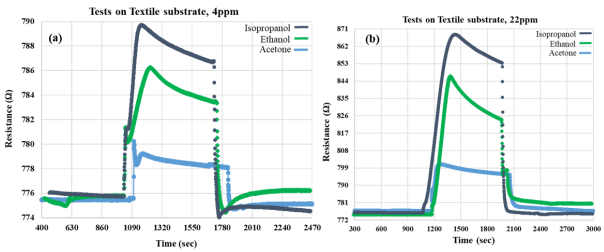

Fig. 6 Sensing results on textile substrate at (a) 4ppm, (b) 22ppm

on PET substrates require more than 10 minutes to reach back the initial stabilized resistance. Whereas the sensors on the other two substrates recovered to the stabilized resistance approximately in one minute. This behavior could be contributed by the porous structure of the paper and cotton fabric, where the entrapped vapors are quickly desorbed.

V. CONCLUSION

We presented a cost-effective approach towards detection of various VOCs through printed sensors based on a carbon black sensing film. The film was printed on three different substrates to investigate the printability, physical and electrical characteristics of the printed layers and ultimately performance of the sensors against different VOCs. A comparative study of the different substrates based on printability, sensitivity and response times of the sensors were evaluated. Sensors based on PET substrate produced higher sensitivity, but higher response times make it compromising for the real time monitoring and fast detection. Despite the lower signal response, sensors based on paper and cotton fabric substrates present promising results based on the acceptable responses as well as the response times. Successful implementation of sensors on cotton fabric show promising results It would further be pursued and the intrinsic wearability of the cotton fabric would be exploited to develop conformable sensors, which are suitable for wearable gadgets.

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reflect the work and are solely the responsibility of the authors.

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