Flexible and highly sensitive humidity sensors using screen-printed TiO2 nanoparticles as sensitive layer

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Abstract. In this work, we present an original example of flexible and miniaturized humidity sensor using screen-printed TiO₂ nanoparticles as sensitive layer. The proposed sensors operate under room-temperature conditions and exhibit high sensitivity to changes in relative humidity. The humidity sensor consists of a TiO₂-based sensitive nanomaterial printed on the top of interdigitated electrodes (IDEs) patterned by laser ablation on flexible substrate. A TiO₂ screen-printing paste from commercially-available nanopowders was developed in order to allow large-scale fabrication of humidity sensors at low temperature. The I-V characteristic of the sensor shows good linearity and resistance measurements confirm the water vapour’s absorption on the sensitive layer, showing high sensitivity in the range of 24 to 90% relative humidity, while exhibiting relatively fast response and recovery times, without the need of any refreshing method.

1. Introduction

Humidity sensors find applications from semiconductor manufacturing to soil moisture monitoring or in food industry and are generally fabricated on ceramic and silicon substrates. Nevertheless, recent advancements in the field of printed electronics show increased potential in substitution of rigid substrates by flexible substrates, due to their low cost and easy fabrication processing.

In parallel, semiconducting metal oxide nanostructures such as TiO₂ nanoparticles, SnO₂ nanowires, or ZnO nanorods have been reported to be good candidates for highly sensitive and stable humidity sensors due to their high surface-to-volume ratio [1][2][3]. Nevertheless, their integration in printed sensors fabricated on flexible substrates is still non trivial, since plastic substrates deform or melt at temperatures of only 100–200 °C [4], which makes them incompatible with the standard silicon and ceramic technologies. Lots of studies have focused on the fabrication of flexible electronic devices using metal oxide materials with good electrical and optical properties [5]. However, their integration as highly-sensitive materials into flexible chemical sensors is still lacking, since they are generally deposited by drop-casting or spin-coating methods [6] which cannot be consider for the mass-production of sensors. One of the main challenges is then the development of cost-effective and low temperature fabrication process allowing the large-scale production of flexible sensors with high performances.

In this work, we demonstrate the feasibility of screen-printed TiO₂ sensing material at low-temperature for the large-scale fabrication of humidity sensors on flexible substrate. The humidity sensors proposed and realized in this work show a high sensitivity in the range of 24 to 90% relative humidity and fast response and recovery times.
2. Materials and methods
A resistive transducer was chosen for the conception of the humidity sensor because it has a simple structure, a low fabrication cost, and it does not require complex read-out circuitry. Typically, it consists of a TiO$_2$-based sensitive nanomaterial deposited on top of gold interdigitated electrodes (IDES) patterned on a flexible substrate.

As a principle, the absorption of water vapour by the sensitive film creates an increase of film electrical conductance due to the dissociation of water molecules to ionic functional hydroxyl groups resulting to a resistance change between interdigitated electrodes which can be easily measured.

2.1. Materials
TiO$_2$ nanoparticles-based paste was used as sensitive layer and was developed for the screen-printing process. Water was chosen as the main solvent of the paste because it is cheap, environmental friendly and it can be evaporated at low temperature.

First, HPMC (hydroxypropylmethyl cellulose) was dissolved in water to increase its viscosity. Next, the resulting water/HPMC solution was mixed with a mixture of propylene glycol/propanol. In parallel, dispersant (Solspers 40000) was dissolved in a mixed solvent of water/propylene glycol/propanol, and TiO$_2$ powder (anatase, sigma Aldrich) was added to the solution. Afterwards, the dispersion was performed by ultrasonication for 20 min. The suspended TiO$_2$ nanoparticles suspension wereas added to the solution of HPMC in a ratio of 1:1 under vigorous stirring at RW20 in 2000 rpm during 20min, to give a final formulation.

2.2. Fabrication process
Keeping the intended final application closely in mind, we aimed to for the development of a simple and economic process for the fabrication of humidity sensors, in order to be able to preserve their attractiveness as low-cost, potentially mass-produced devices. The fabrication process of the sensors proposed in this work is fast, compatible with rolls-to-rolls technologies and does not require the high-cost semiconductor manufacturing equipment and high temperature steps normally used for silicon or ceramic microfabrication. It combines a laser ablation technique for the fabrication of the micro-scale electrodes and a screen-printing process for the patterning of the TiO$_2$ nanoparticles-based sensing material. The process sequence is illustrated in Figure 1.

![Figure 1: Process sequence of the humidity sensors: (a) Cleaning of the PET substrate. (b) Deposition of the gold layer by electron beam evaporation. (c) Laser ablation of the gold layer. (d) Screen-printing of the TiO$_2$ nanoparticles.](image)

Initially, a commercial PET flexible substrate of 50 µm thick was cleaned with iso-propanol and dried at 80°C for 15 min. Next, a gold layer was deposited on the substrate by electron-beam evaporation. Afterwards, the resulting layer was directly patterned by laser ablation (Nd:YAG-1064 nm, Rofin) in order to create micro-scale interdigitated electrodes using a process inspired from [7]. The TiO$_2$ nanoparticles-based paste was then patterned on the surface of electrodes by screen-printing (EKRA 2H screen printer) which is a widespread industrially-applied method. A screen made of photosensitive film of 50 µm thick and a mesh of 40 µm thick were used to successfully achieve the deposition of the sensing material. Finally, the resulting devices were dried at 80°C for 30 min in an oven to accelerate the solvent evaporation. Note that the solvent evaporation can be also performed at room temperature during 1 day.
This process has the advantage to be fast and cost-effective; it allows also the mass-production of humidity sensors at low-temperature. In addition, due to their small size, the resulting devices can be easily integrated in a microchip for industrial use. The characterisation of the resulting humidity sensors is described in the following parts.

3. Results

3.1. Characterization of the device geometry

Using the process described above, the large scale fabrication of humidity sensors has been successfully achieved. Figure 2a shows a matrix of 3x3 sensors. The interdigitated electrodes are 600 μm long and 60 μm wide, and they are separated by a gap of 50 μm (Figure 2b). Here, small electrode geometry was obtained compared to the standard printed sensors generally above 100 μm which is very important for resistive-type sensor performances [8].

The screen-printed TiO₂ nanoparticles layer forms a rectangle of 1 mm wide and 1.5 mm long covering perfectly the surface of electrodes (Figure 2c).

![Figure 2](image)

**Figure 2**: (a) Matrix of humidity sensors fabricated on PET substrate. (b) Optical image of the interdigitated electrodes before the deposition of the TiO₂ nanoparticles. (c) SEM (scanning electronic microscope) picture of the TiO₂ layer screen-printed on the surface of electrodes.

3.2. Electrical characterization

Figure 2a shows the I−V characteristics of the humidity sensor and the patterned electrodes without coating of the sensitive layer measured at humidity levels of 12% and 40% using semiconductor parameter analyser. In Figure 3a, we can observe that the current did not flow on the unprocessed substrate implying that the PET substrate is an insulator. The I−V characteristics of the device with TiO₂ nanoparticles show Ohmic behaviour in both conditions, at 12% RH and 40% RH (Figure 3b). The resistance is constant over the supply voltages; the sensitivity is then identical regardless of the operation bias. In other words, a low voltage operation does not hinder the sensitivity which is essential for low power operation.

![Figure 3](image)

**Figure 3**: I−V characteristics measured under humidity levels of 12% and 40%. (a) for a device without TiO₂ deposited on the electrodes, and (b) for a device with TiO₂ nanoparticles.
3.3. Humidity sensing properties
The humidity-sensing performances of the TiO$_2$-based sensors were investigated under various levels of relative humidity (RH) in a climatic test chamber with a control module (Hygrometer testo 608-H1) and at room temperature conditions (26°C). Figure 4a shows the sensor response when the relative humidity in the chamber was sequentially changing from 12% to 52% in periods of 10 min. The response curves are almost identical at a given humidity indicating repeatability of the results with a fast response time and almost immediate recovery. Figure 4b shows the resistance changes when the sensor was placed in different humidity conditions. In this figure, we can see that low concentration of humidity (24%) can be measured proving the ability of the sensors to be used for accurate humidity detection.

![Figure 4: (a) Repeatability curves of the humidity sensor for humidity level variations from 12% to 52%. (b) Resistance changes of the sensor as function of the relative humidity.](image)

4. Conclusion
The large-scale production of humidity sensors on flexible substrate was successfully achieved using a laser ablation method for the fabrication of micro-scale electrodes and a screen-printing technique for the patterning of the TiO$_2$-based sensing material. Both methods are fast, cost-effective, and compatible with flexible substrate. This approach addresses the technological barriers that can hamper the development of chemical sensors on flexible substrates. In addition, the resulting humidity sensors exhibit high sensitivities in the range of 24 to 90% relative humidity and fast response and recovery times, which paves the way to large-scale fabrication of printed sensors on flexible substrate.

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