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Inkjet and microcontact printing of functional materials on foil for the fabrication of pixel-like capacitive vapor microsensors

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ABSTRACT

The work presented demonstrates the utilization of micro-contact printing of self-assembled monolayers (SAMs) of gold nanoparticles (NPs) to pattern the porous thin metallic film composing the top electrode of an ultra-fast capacitive relative humidity sensor based on miniaturized parallel-plates electrodes. The rest of the device, which occupies an area of only 0.0314 mm^2, is fabricated by inkjet printing stacked individual drops of functional materials, namely gold NPs for the bottom electrode and a polymeric humidity sensing layer, on a polymeric foil. Compared to other printing methods, the use of microcontact printing to pattern the top electrode enables the additive transfer of a solvent-free metallic layer that does not interact chemically with the sensing layer, permitting the thinning of the latter without risk of short-circuits between electrodes, and broadening the range of usable sensing materials for detection of other gases. Thinning the sensing layer yields to ultra-fast response devices with high values of capacitance and sensitivity per surface area. The fabrication process is compatible with low heat-resistant polymeric substrates and scalable to large-area and large-scale fabrication, foreseeing the development of low-cost vapor sensing sheets with high space–time resolution, where every sensor would correspond to a pixel of a large array.

1. Introduction

Printed electronics enables ultra-low-cost patterning on a variety of large-area organic and inorganic substrates. Thus, it presents itself as a perfect complementary approach to the traditional methods for microelectronics fabrication. The additive character of printed electronics, combined with its compatibility with on-foil fabrication at large area and high-throughput by means of roll-to-roll [1,2], renders it the best candidate for a number of new applications demanding large area, low-cost per surface area, light weight and mechanical flexibility, such as artificial skin [3–5] or smart packaging [6]. As a consequent, printed sensors based on electronic components are becoming increasingly popular. A proof of it is the number of works reporting printed biosensors, pressure/strain sensors, thermoresistors and resistive and capacitive gas sensors on plastic foil that have been published in the last years [7–12]. The majority of the mentioned works utilized inkjet or gravure as printing techniques. Both techniques are well known since they have been widely used in graphic printing for decades, resulting in the existence of commercially available, performing and readily usable printing equipment. However the resolution allowed by inkjet or gravure printing is still not comparable to the resolution achievable using photolithography. The development of alternative printing methods that combine the resolution

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of photolithography with the throughput and additive character of classic printing methods has been a matter of study in the last decade. One example of the progress of this field is microcontact printing. Microcontact printing is a sophisticated version of stamping where the molecules to be printed are adsorbed on the stamp surface during inking and transferred to the substrate due to physical or chemical interactions during printing, rather than being absorbed in the stamp during inking and diffused onto the substrate during printing as in traditional stamping [13]. The stamp is often an elastomer with a relief pattern fabricated by standard microelectronics methods [14]. Since its first presentation in the early 1990s by Kumar and Whitesides [15], microcontact printing has been used to transfer SAMs of organic molecules such as thiol or silanes onto different substrates to define electroplating masks for the fabrication of transistors [16–20] or to transfer tight SAMs of gold NPs for the fabrication of the gate of flash memories [21], among other applications. However, only few examples can be found where this printing method has been used to pattern directly electrically conductive lines (or precursors) [16], useful for the development of actuators and sensors.

Capacitive gas sensors present certain advantages compared to other gas detection methods such as lower power consumption and higher selectivity [22,23]. CMOS-compatible capacitive gas sensors consisting of a silicon capacitor with a specific sensing layer have been widely studied [22,24–27]. Also, recently some research groups have expanded the field of capacitive gas sensors to foil substrate, maintaining the use of standard technology for patterning [28,29]. It has been only over the last 5 years, when some examples of printed (mainly inkjet and gravure) capacitive gas sensors have been reported [9,12,23,30–33]. The most part of the aforementioned works were based on interdigitated electrodes (IDE) to facilitate post-fabrication coating. However, despite its processing limitations, parallel-plate geometries present clear advantages in terms of sensitivity [26,33] and the non-parasitic effect of the substrate in the capacitance signal, which involves the need of using differential measurements to obtain the net signal of the sensing layer [23,28]. On top of that, the lower resolution of standard printing methods compared to photolithography, worsen even more the performances of the existing printed IDE sensors. On one hand, it has been demonstrated that the thickness of the sensing volume in IDE capacitive gas sensors coincides with the pitch of the IDE for maximum sensitivity [34,35]. The response time of such sensors, which depends on the diffusion of the analyte in such sensing volume, evolves then quadratically with this thickness [25,27,36]. Hence, IDE printed with large pitch due to low printing resolution results in sensors facing a trade-off between good sensitivity and short response time. On the other hand, since the nominal value of IDE capacitors is proportional to the number of electrodes and their length, highly-spaced printed IDE capacitors supply little capacitance per surface area, requiring devices of few square centimeters to supply the few pF necessary for their read-out with the most part of standard electronic chips [29,37]. To surmount the aforementioned issues in printing capacitive gas sensors, our group has previously reported on fully inkjet-printed parallel-plates capacitive humidity sensors on foil [33]. The devices presented a 7.5 μm-thick humidity sensing layer of cellulose acetate butyrate placed between silver parallel electrodes. The devices, with a surface area of only 1 mm^2, provided a capacitance of 3.5 pF. The patterning of gas intake windows on the top electrode, required for evaporated devices [26,27,38], was not necessary for these printed devices due to the lack of continuity of the top electrode resulting from the high roughness of the printed sensing layer and the porous nature of printed nanoparticulated metals [39–42]. This fact alleviated the requirements of patterning resolution of the top electrode permitting, in theory, the potential reduction of the surface area, A, of the printed sensor. Nonetheless, to maintain a fixed capacitance value, the thickness of the dielectric sensing layer, t, should be reduced at the same rate according to the well know expression $C = \varepsilon_0 \varepsilon_r A/t$ (where ε_0 and ε_r are the electrical permittivity of vacuum and sensing layer respectively). Furthermore, the thinner the sensing layer, the faster the response time of the sensor. However, thin sensing layers increase the risk of shortcircuits between top and bottom electrode unless the solvent of the top electrode is chemically orthogonal to the sensing layer material, reducing the materials choice and the associated range of potential applications of the sensors.

In this work, we demonstrate the miniaturization of printed parallel-plates capacitive gas sensors by decreasing their size down to the surface area occupied by single drops of 10 pL of gold, inkjet-printed on PEN foil (i.e., 200 μm of diameter). Such reduction in size was possible without significant loss of capacitance per surface area due to the thinning of the inkjet-printed sensing layer to less than 1 μm. The thin sensing layer was also the responsible of the fast operation of the devices. Minimizing the risk of shortcircuits between top and bottom electrode was achieved for such thin sensing layers by utilizing, for the first time, microcontact printing of solvent-free self-assembled monolayers (SAMs) of gold nanoparticles (NPs) to pattern the top electrode. The transfer of the top electrode was carried out using a pre-patterned elastomeric stamp, and nitrogen plasma was employed afterwards to render the electrode electrically conductive at room temperature. The absence of solvents and high temperatures during the fabrication of the top electrode makes the process potentially compatible with a broad range of sensing materials. We assess the validity of this fabrication method by developing a relative humidity (R.H.) sensor consisting of stack printed layers of gold (bottom and top electrode) and humidity-sensitive cellulose acetate butyrate. The developed sensor is the smallest printed humidity sensor reported up to date with an area of 0.0314 mm^2. The signal of the sensor displayed linear dependency with relative humidity, and outperformed previously reported printed humidity sensors in terms of response time and sensitivity per surface area. The proposed method leaves an open door to further miniaturization by optimizing the topology of the printed sensing layers. The outcome of this work pave the way to very low-cost and performing devices on flexible and light-weight substrates, and foresees the possibility of detecting precise gas concentration