Microelectronic Engineering 119 (2014) 11–15

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Chemocapacitive sensor arrays on Si substrate: Towards the hybrid integration with read-out electronics

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ARTICLE INFO

Article history:
Available online 19 February 2014

Keywords:
Chemocapacitors
Microfabrication
Chemical sensing
Polymer

ABSTRACT

Chemocapacitors, i.e. capacitors where the dielectric layer is a polymeric layer with selective sorption of certain analytes, are extensively used in the monitoring of the environmental humidity and of other volatile analytes. The specifics of the detecting mechanism have been found to rely on a combination of interactions arising from vapor sorption, polymer swelling, and morphology changes. The aim of the present work is to develop a fabrication procedure of InterDigitated Electrodes (IDEs) with high sensing performance. The IDEs layout has been optimized in terms of sensing performance and is in accordance with the read-out electronics specifications. The realization and evaluation of chemocapacitor arrays integrated with read-out electronic module in the presence of various analyte vapours is demonstrated in laboratory environment. The analytes employed in the present study are typical for the printing industry of flexible packaging.

1. Introduction

The field of gas sensing devices for monitoring the composition of the gaseous environment in real conditions where humidity and temperature variations occurred has attracted the interest of several research groups [1] and companies [2–6]. A solution in order to be useful for potential application in real conditions should meet a number of diverse specifications that are related to the size, the weight, the energy consumption, the maintenance needs, and the cost. Such systems could furthermore form sensor networks for long term continuous and wireless sensing application such as monitoring the gaseous environment of large working areas e.g. industrial plants. The use of standard microelectronic/micromachining processing allows the realization of gas sensing systems based on several transduction principles that are in principle facilitating the accomplishment of these goals. The implementation with circuitry in complementary metal oxide semiconductor (CMOS) technology [7–9] with particular emphasis in sensors or sensors arrays based on metal oxides [6,10], acoustic waves [4,11], cantilever resonance [2,12], resistance changes-chemoresistors [3,13,14] or capacitive changes-chemocapacitors [5,15,16] is usually the key components.

The sensor or the sensors array should be appropriately designed for the targeted application and ideally should be either monolithically integrated with read-out electronics or hybrid integrated with commercially available ones. In this direction the use of chemocapacitor type sensors is promoted, with already proven promising results in terms of selectivity/sensitivity and reproducibility with potential application in measurements of complex gaseous environments [15,17], without the need of pretreatment units [18] or costly sensing materials [19].

Generally, chemocapacitors are capacitors where the dielectric layer is a polymeric layer with selective sorption of certain analytes. Several electrode configurations have been proposed with the configuration of planar InterDigitated Electrodes (IDEs) to be the most promising since it addresses the need of feasible fabrication and manageable disposal of the polymeric sensing material [20].

In most cases the IDE structures are fabricated on dielectric substrates such as glass or quartz or flexible polyimide foils [21,22]. On the other hand in the case of Si substrate which has the obvious advantage of using available fabrication technologies, the layout of choice is the one of parallel plates capacitor where the top electrode is perforated to allow for interaction

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http://dx.doi.org/10.1016/j.mee.2014.02.007
0167-9317/

between the analyte-target of the gaseous environment and the polymeric layer [23]. This approach has however certain technological constraints in terms of capacitor fabrication i.e. the application of the sensing polymeric layer to fill the gap between the two electrodes and the extended response time due to the limited surface for interaction between the polymeric layer and the environment.

In the present work we deal with the following tasks: (i) the fabrication of miniaturized IDE arrays on Si wafer through standard micromachining/microelectronic processing, (ii) the optimization of layout dimensions to meet the read-out electronics specifications (iii) the realization and evaluation of the sensing system, consisting of chemocapacitor arrays of different IDE layouts, in the presence of different concentrations of ethyl acetate, alcohol and humidity in laboratory environment and (iv) the comparison between the responses from chemocapacitors with simulation data obtained by a previously implemented generic model [21]. Emphasis is given here on the integration of the miniaturized sensor array with commercial read-out electronics. However, our interest in the particular Volatile Organic Compounds (VOCs) stems from an on-going project on the development of a holistic system based on wireless sensor network meeting all the specifications outlined above, for the continuous monitoring of the gaseous environment in printed flexing packaging industries. In particular, a major ink solvent used in printing technologies such as flexographic or rotogravure printing, is ethyl acetate, mixed in certain cases with low molecular weight alcohols.

2. Fabrication of the sensor array

The IDEs, consisting by two interpenetrating comb metallic electrodes, are defined by the electrodes width (W) and the gap width (G) between the electrodes and are fabricated on Si wafers with a thick dielectric layer on top. It is crucial for the design of IDE layout to ensure that the thickness of the dielectric layer should be higher than half the spatial periodicity ($\lambda = 2(W + G)$) of the metallic electrodes in order to avoid the penetration of the electric field below the substrate [24]. Thus short-circuit effects and cross-talk between chemocapacitors on the same chip are eliminated. The optimum IDEs layout design was selected after theoretical studies investigating the feasible fabrication, without cost in the manageable disposal of the polymeric sensing material on the sensing area, in conjunction with the gain in terms of sensitivity as electrodes critical dimension is miniaturized. The latter will be discussed in the sections above.

The detailed fabrication flow-chart of the IDE arrays with critical dimension 1.0 μm W(=G) on Si wafers through standard micromachining/microelectronic processing is illustrated in Fig. 1.

At an early stage a Si wafer is thermally oxidized at a thickness of 3 μm. The SiO_2 layer should be of such high thickness in order to prevent any potential cross-talk between adjacent capacitors. Then the PMMA/PEDOT:PSS bi-layer is spin coated followed by an e-beam lithography (EBL) step. The PEDOT:PSS conductive polymeric film is used as charge dissipation layer. Charging of non-conducting materials during electron beam writing is a common phenomenon leading to deflection of the electron beam and resulting in pattern distortion. This effect is caused from the charge that builds up in the materials stack during the electron beam exposure and depending on the conductivity of the stack, it can reach to sufficient levels to bend the electron beam [25]. In the presence of a conducting layer i.e. PEDOT:PSS, the charge build up can be reduced significantly [25,26]. After e-beam exposure the PEDOT:PSS layer is removed in a water rinsing step followed by PMMA development in IPA:H_2O 7:3 solution at room temperature. A flood exposure step in Deep Ultraviolet (DUV) radiation is applied for chain scission of eth remaining PMMA features in order to facilitate the subsequent lift-off step. Then an Al layer of 200 nm is deposited via sputtering followed by ultrasonic assisted lift-off in acetone guarantying functional IDEs over very large areas. After the realization of the IDE structures, a well of 50 μm thick negative epoxy resist layer (SU-8 3050 [27]) is formed around the IDE areas through standard I-line processing. Technical details about the fabrication processing steps are presented in Table 1. In Fig. 2 a SEM image of an IDE structure and the appropriate SU-8 thick well for the enclosure of the polymeric material in the sensing area is displayed. Finally several semi-selective polymeric materials are deposited on the IDEs sensing areas, of an 8-InterDigitated Capacitor (IDC) sensor array.

3. Adjustment to read out electronics on the basis of the IDE design selection

As we mentioned above the selection of the IDE layout, i.e. finger width, finger gap and sensing area was based on a generic model developed by our group for the estimation of the capacitance values of different IDE layout configurations in relation with the dielectric permittivity of the, either dry, or interfacing with analyte-targets, sensing material [21,28]. Evaluation of the simulated data for IDEs with same metallization ratio ($\eta = W/(W + G)$) showed that miniaturization of the critical dimension (W(=G)) results in increased sensitivity.

The same simulation data showed that the sensitivity is approximately the same for the 1.0 μm W(=G) and 0.5 μm W(=G) IDEs layouts (a slight enhancement occurred with further miniaturization). The simulation data are presented in Table 2 and are taken from Ref. [21].

Moving towards the hybrid integration of such a miniaturized sensor array with commercial available read-out electronics certain limitations should be taken into account. Based on previous studies focusing in the direction of fabrication of a hybrid gas sensing module [15] where certain read-out electronics circuits were used, an initial capacitance value of 10 pF is the most compatible and the appropriate detectable range scale is 0–21 pF. Consequently, in order to meet this particular specification, miniaturization of the electrode's critical dimension requires the miniaturization of the sensing area of the IDEs layout. For example for initial capacitance of 10 pF, an area of 0.7 mm^2 is needed for 1.0 μm W(=G) while for the case of 0.5 μm W(=G) layout the area should be 0.20 mm^2. Decreasing of the sensing area at the value of 0.2 mm^2 introduces difficulties to the uniform coating of the polymeric material with simple laboratory conditions i.e. spin coating or drop casting. In such a case, special equipment is needed.

Concluding, further miniaturization than 1.0 μm W(=G) layouts contributes only to minor enhancement of the sensitivity while the resulting reduction of the sensing area in order to meet the read-out electronic specifications is restrictive due to fabrication constraints.

4. Realization and evaluation of sensing systems

A sensor array consisting of 8-IDEs with critical dimension of 1.0 μm W(=G) is coated with several different polymeric materials and is integrated with an electronic module that allows for the operation, control and data transfer to a PC or other unit with data storage and processing capabilities [15]. The polymers were selected on the basis of different selectivity to the vapor analytes of interest (EtOH:ethanol EtOAc:ethyl acetate and water). In particular, studies on the pervaporation of water–ethyl acetate mixtures through the dense poly(dimethylsiloxane) (PDMS) membranes