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Flexible Approach to Sensors Arrays Nanopatterning for Real-Time Water Contaminants Monitoring Platform

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Abstract. This paper reports on the development of a flexible nanopatterning approach using the NanoeNabler™ to manufacture miniaturised sensor arrays platform for real-time water quality assessment. Traditionally biosensors are fabricated by lithography, screen printing, inkjet printing, spin- or deep-coating methods to immobilize the sensing element onto substrate pre-patterned with electrodes. NanoeNabler™ patterning method is benchmarked against other currently adapted approaches for cost-effective sensors arrays manufacture. Sensors measuring ~1 µm diameter or more can be patterned for further employment in molecularly imprinted polymer structures. Notably, the dimensions of the sensor depend on the fluid being patterned and on the interaction forces between the substrate and the patterning tool. Thus, careful selecting of patterning parameters is vital for repeatable and controlled manufacture of sensors to guarantee superior sensitivity. The reported nanopatterning method is capable of accurately placing attoliter to femtoliter volumes of liquids, including proteins and DNAs, onto any substrate, thus making it an ideal technology for biomedical sensors. A custom-made 1 cm² silicon wafer with 48 interdigitated electrodes sensor heads was used as a platform for the multi-sensor array with potential use in a wide range of real-time monitoring applications.

Introduction

Amperometric, potentiometric and conductometric sensing approaches are widely used in the measurement of pollution in water [1]. The sensors change their properties as a result of interaction with the component being measured, i.e. depending on the composition of water. The species of interest are either oxidised or reduced at the working electrode causing a transfer of electrons, thus generating a measureable signal. This change can be recorded as a change in the output signal, i.e. output voltage, current, change in conductivity, capacitance or dielectric constant – whatever parameter gives the most pronounced sensor response [2].

For example, a portable amperometric three-electrode immunosensor for screening of polycyclic aromatic hydrocarbons (PAHs) in water was recently reported [1]. In particular, amperometric detection is based on the measurement of current when a potential is applied to the working and reference electrodes of the system.

Traditionally sensor arrays are fabricated by lithography, screen printing, inkjet printing, spin- or deep-coating methods to immobilize the sensing element onto a substrate pre-patterned with electrodes. There is a considerable interest in manufacturing sensor arrays with miniaturised dimensions for an extensive range of applications, such as medical diagnostics, drug discovery, environmental and gas monitoring and so forth. One of the novel technologies that offers this opportunity is nanopatterning via BioForce NanoeNabler™. It opens new horizons for the development of nanosensors and nanoprobes with micron or submicron dimensions that are suitable for cells or intracellular measurements, and therefore is the perfect choice for fabricating the nanoscale biosensor arrays.

Traditional direct printing methods used for sensors arrays manufacture

Inkjet printing technology can be divided into two broad categories: drop-on-demand inkjet (DOD), where droplets are generated only when required, and continuous inkjet (CIJ). In CIJ droplets are ejected continuously from the print head, and then are either directed to the substrate as printing drops or to a collector for re-circulation and re-use [3]. Inkjet can be further subdivided according to the specific means of generating droplets, such as piezoelectric and thermal technology.

Ink-jet printing is a versatile technique that has been widely used for the non-contact writing of two dimensional features and less widely but increasingly, for three-dimensional structures. The mild environments afforded by ink-jet printing make it particularly suited for handling biological samples, since contamination can be minimized and waste be reduced. Another advantage is the accurate placement of pre-determined quantities of material, which can be performed without the need for previous patterning steps [4-7]. Piezoelectric inkjet printing of polymers and proteins holds great promise for fabrication of miniaturized bioelectronic devices, such as biochips and biosensors, and was recently employed for the development of a glucose biosensor [8]. Inkjet printing is in line with industrial needs for robust, high volume and precise deposition of advanced liquid solutions including containing photocatalytically active TeO_2 nanoparticles [5].

Screen-printing thick-film technology has emerged as a cost-effective method for the production of sensors, since silicon based approaches are only feasible if the volumes produced are high. For low to medium scale manufacturing, particularly where the application is highly specialised, thick film sensors are more suitable because they are robust, can be miniaturised and integrated onto the same substrate as the electronics. A further advantage of this approach is that a wide range of materials can be fused together to form a device with the required properties and in some cases, the need for solder joints can also be eliminated. The screen-printer forces an ink or paste using a squeegee through a stainless steel mesh onto the substrate to form an image, as it is shown in Fig. 1.

It is more frequently employed in sensor fabrication than photolithography for its precision, speed and low cost. There are a number of key processes that determine the performance of thick film sensors, namely composition of the paste that will form the sensing layer, printing process parameters and drying/firing conditions. Detailed manufacture procedure of a miniaturised screen-printed pressure sensor can be found in [9].

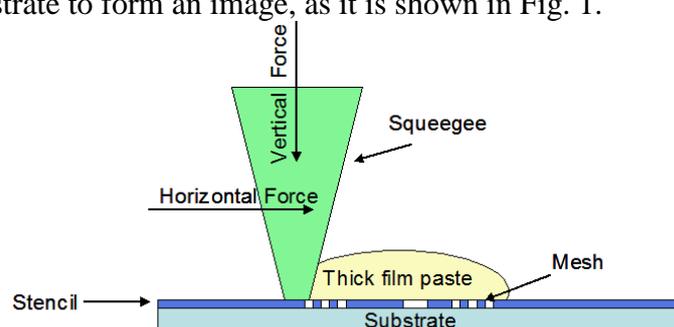


Fig. 1. Schematics of a screen-printing process.

Fabrication of microsensor arrays using novel nanopatterning approach

Novel nanopatterning technology offered by BioForce NanoenablerTM was successfully tested for developing various microsensors arrays. This system uses a liquid dispensing process via specially designed surface patterning tool (SPT), which is microfabricated cantilever with an integrated passive microfluidic system, capable of controlled deposition of attoliter to femtoliter volumes of DNA, proteins, and other molecules on a wide variety of surfaces. This instrument platform (Fig. 2) consists of supporting hardware components, an easy-to-use software controller interface, and an array of tools that permit real-time observation of the printing process.



Fig. 2. BioForce NanoenablerTM.

Fluid loaded into the reservoir flows down the microchannel by capillary flow until it reaches the gap at the end of the SPT. During the deposition process, which typically takes less than 100 msec, SPT end touches the surface and a volume of fluid is instantly transferred with a high degree of spatial accuracy. It is strongly believed that the reduction in the size of surface immobilized assays creates new opportunities in areas of chemical and biological sensor development.

A custom-made 1 cm² silicon wafer with 48 interdigitated electrodes sensor heads was used as a platform for the multi-sensor array with potential use in a wide range of diagnostic applications. The detailed description of a process for the manufacture of microscaled interdigitated electrodes for sensors array can be found in [10]. Fig. 2 a) illustrates CAD layout of the resultant electrodes arrays, whereas Fig. 2 b) is an optical image of 12 sensor heads within the array. The width of each electrode is 2 μm .

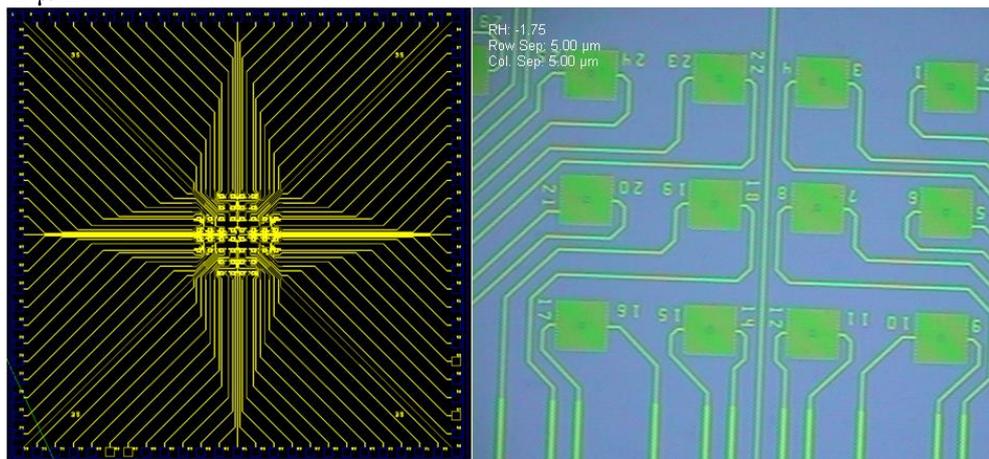


Fig. 2. a) CAD layout of the chip; b) Optical image of 12 sensor heads within the array.

While printing freshly prepared cytochrome oxidase solution, the parameters were set to maintain the printed droplet diameter at approximately 18 μm (Fig. 3 a)). The key parameters that affect the printability of the solution are its composition, the contact time and force, and the duration of UV-ozone treatment to achieve the hydrophilic surface. Once the parameters are properly chosen to suit particular substrate and solution, hundreds of sensor arrays can be printed in a single process (Fig. 2 b)), making this technology a favourable option for biomedical applications when miniaturization, precise positioning and repeatability are the key requirements. The print contact time was maintained at 0.5 s and the UV-ozone exposure of the wafer before patterning was ~ 40 min.

Solution of cytochrome oxidase was printed over the arrays of interdigitated electrodes and the resultant sensors were tested in 100 Hz – 10 MHz frequency range using HP 4192A Impedance Analyzer. Then at a chosen frequency of 100 kHz a capacitance versus time was monitored. At a certain point a drop of ethanol solution was placed over the sensor head and an instant response, namely a decrease in the value of capacitance from 6.35 pF to 5.87 pF, was recorded.

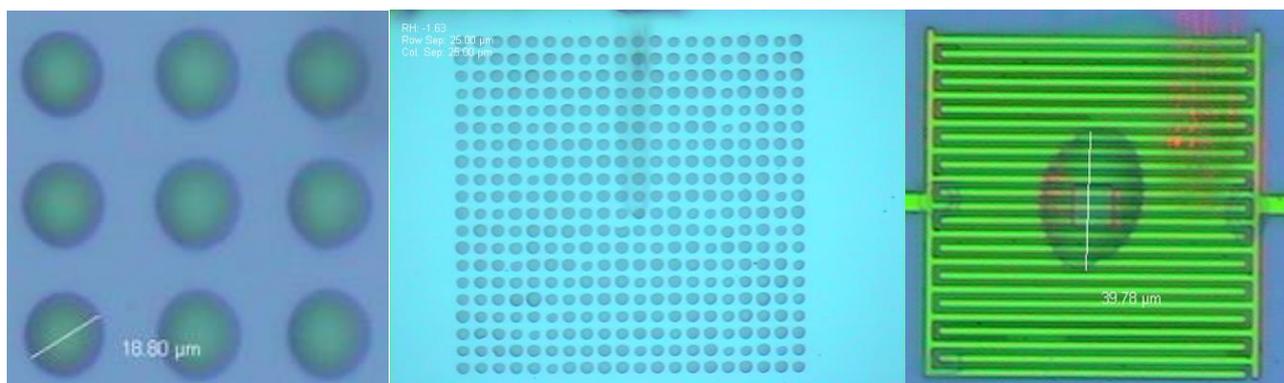


Fig. 3. a) Sensor heads ~ 18 μm diameter; b) 20 x 20 sensors array; c) single sensor head.

Summary

This work demonstrates that nanopatterning via Nanoenabler™ is a practical technique for cost-effective, microscale and reproducible sensors arrays manufacturing. The Nanoenabler™ system offers the direct transfer of fluidic materials onto various surfaces for a variety of novel applications, including real-time monitoring of water pollutants. This method was successfully verified by testing the response of cytochrome oxidase to ethanol, which occurred in real time and resulted in a decrease in the value of capacitance from 6.35 pF to 5.87 pF.

Acknowledgment

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