

Heterogeneous Integration of Nanowires for Chemical Sensor Arrays

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Project Objectives

Nanoscale chemical sensors offer great promise for use in cross-reactive arrays because of their inherent high sensitivity, low power requirements, and potential for massive redundancy. Electronic “noses” employing macroscale sensors have previously been used for such diverse applications as determining breath alcohol levels, automotive exhaust safety inspection, identification of toxic gases, and wine classification. The primary disadvantage of macroscale sensors, however, is their inability to detect analytes in a power- and area-efficient manner, and to be integrated conveniently into chips that combine the functions of chemical sensing and signal processing. This project seeks to address this problem by developing sensory materials that can be integrated into two platforms: high aspect ratio nanowires that contain a sensory element within the wire, and nanospheres that contain a sensory coating. Dielectrophoretic and microfluidic techniques are used to integrate these sensory wires and beads into simple test circuits for characterization of the sensor response. The ultimate goal of the project is to use the same heterogeneous integration techniques to create very large cross reactive arrays of sensors. These arrays will be coupled to an underlying VLSI pattern classifier, the development of which is being pursued in parallel with the sensor synthesis, characterization, and assembly tasks.

Results

We have developed methods for growing nanowires containing conducting polymer “stripes” between metal (typically Au) ends. The length of these nanowires is a few microns, and the diameter can be varied between about 40 and 300 nm. An important aspect of this work is to develop a diverse set of sensor elements based on different conducting polymers, covalent modification of the polymers, or incorporation of molecular recognition groups by ion exchange. We have fabricated nanowires containing different conducting polymers (poly(pyrrole), polythiophene, and poly(ethylenedioxythiophene)), and has also incorporated proteins (avidin, streptavidin, catalase) into the polymer segments with retention of their molecular recognition (of biotin) and catalytic (peroxide decomposition) functions. The biotin provides a “hook” for binding other specific sensory or catalytic receptors.

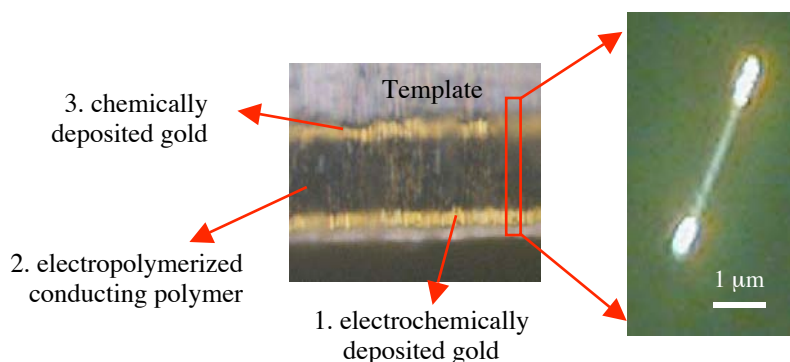


Figure 1. Electrochemical replication of porous templates (in this case an anodic alumina membrane) gives free-standing nanowires containing polymers, polymers containing embedded proteins,² or metal oxides³ between metal end contacts. This procedure typically produces 10^8 - 10^9 nearly identical nanowires in a single experiment.

A second type of sensor element incorporates a thin layer of the sensory polymer as a shell on the surface of silica nanoparticles. These silica particles are highly monodisperse and can be made with diameters ranging from 35 to 1500 nm. In this case, layer-by-layer assembly rather than electrodeposition is typically used to deposit the sensory shell material.

The nanowire sensors are being integrated into single wire testbeds using an electrofluidic assembly process illustrated in Fig. 2.⁴ We have employed this technique to design an on-chip test structure that is compatible with a 40-pin dip package used in the chemical sensing characterization system at NIST. An important feature of this assembly process is that it

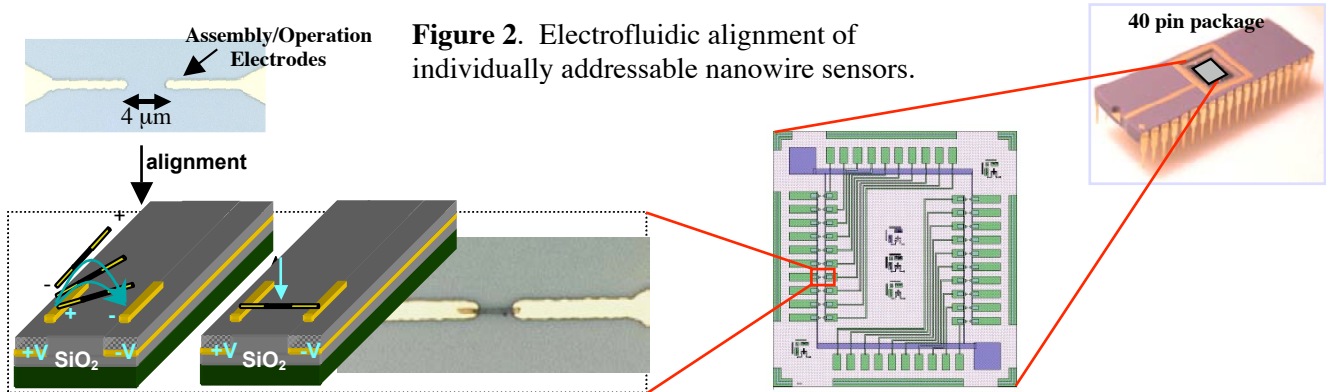


Figure 2. Electrofluidic alignment of individually addressable nanowire sensors.

requires no post-processing once the nanowires are aligned. We have constructed a gas mixing and delivery system that allows us to measure the response of the nanowire sensors in this test bed to volatile analytes and have so far verified the expected electronic responses of PEDOT sensor stripes to vapor phase ammonia and water.

The nanobead sensors are being integrated into a multiplexed cross-point electrical testbed using fluidic assembly processes. In contrast to the nanowire platform in which each sensor is connected to the underlying CMOS circuitry, the nanobeads will be addressed in row-column format similar to that used in dynamic memories. We are currently developing a process strategy that connects the nanosensors between the top and bottom metal electrodes of the cross-point array as illustrated in Fig. 3. Capillary forces push the bead to one side of the well, making the

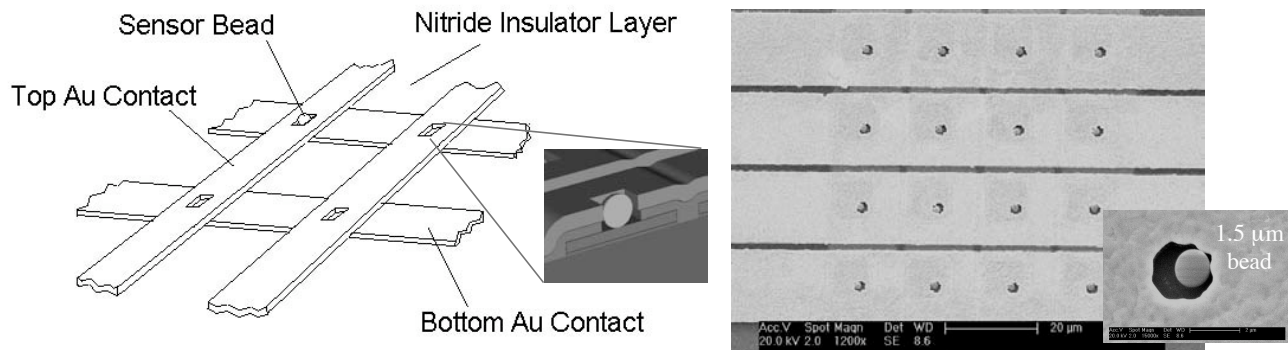


Figure 3. Crossbar structure for integration of sensory nanobeads. *Left and center:* schematic illustration of layout of top and bottom contacts. *Right:* Aligned beads contact the sidewall and bottom of lithographically defined wells.

conducting polymer shell of the bead contact both the top and bottom electrical leads. Our initial assembly results with micron-size beads are quite promising, and we are currently scaling this process into the nano-regime as we characterize the electronic response of larger sensor beads.

An effective cross-reactive sensing system requires a robust pattern classifier that reliably and reproducibly detects gas compounds of interest while operating in environments that differ considerably from the initial training environment. Our current solution to this problem utilizes an on-chip distributed pattern classifier, instead of the off-chip software based solution presented in our earlier work on this project.⁵ As a result, our approach utilizes the underlying silicon area below the sensors more efficiently and provides a complete single chip solution.

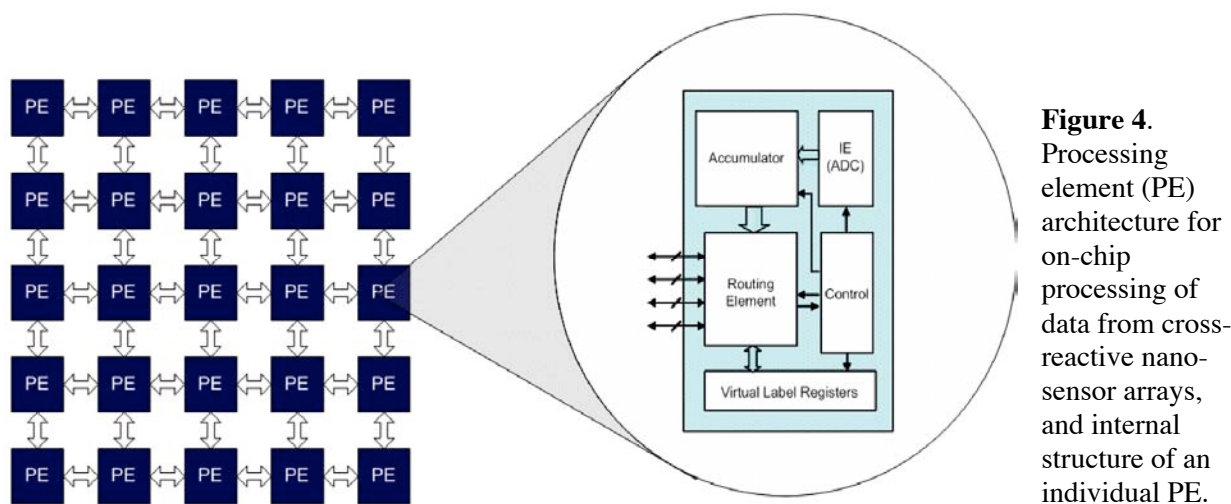


Figure 4. Processing element (PE) architecture for on-chip processing of data from cross-reactive nano-sensor arrays, and internal structure of an individual PE.

Fig. 4 illustrates a pattern classifier architecture based on the Nearest Neighbor classification scheme. The implementation consists of an array of $m \times m$ Processing Elements that maps Gas responses in three dimensions to a register in the 2D Mesh. Each Processing Element, PE, consists of the interface electronics unit, an accumulator, routing unit, control unit and a gas labeling unit. The accumulator sums the responses of all the sensors of each of the three sensor types connected to the PE's interface unit. The routing unit provides communication between adjacent PEs while the gas labeling unit provides the core pattern classification functionality. System operation is divided into two disjoint phases, namely the *Training Phase* in which the original knowledge base of the classifier is formed and the *Detection Phase* during which the knowledge base is referenced to distinguish the presence of gas compounds of interest.

References

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