

Hybrid Polymer/Ultrathin Porous Nanocrystalline Silicon Membranes System for Flow-through Chemical Vapor and Gas Detection

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ABSTRACT

Here we discuss a novel capacitive-type chemical sensor structure that uses recently discovered porous nanocrystalline silicon (pnc-Si) membranes [1] covered with metal as the capacitor plates while a polymer layer sandwiched between them serves as the sensing layer for solvent vapor detection. Pnc-Si is new ultrathin (15 nm) membrane material with pore sizes ranging from 5 to 50 nm and porosities from < 0.1 to 15 % that is fabricated using standard silicon semiconductor processing techniques. We present a study of pnc-Si membranes as a platform for such a sensor. The degree of swelling and the reversibility of the polymer/pnc-Si membrane system exposed to analyte-containing vapors are observed using optical and electrical techniques.

INTRODUCTION

Highly sensitive sensors capable of chemical vapor and gas detection are an increasing demand in industry, medicine and environmental monitoring applications. Polymer based sensors are attractive because of their low cost and the variety of different polymers available for sensing applications. The polymer materials are used as responsive coatings as they are able to selectively absorb different molecules, which results in polymer swelling or a change in its electrical properties.

The transducer elements for polymer-based sensors include chemiresistors that measure resistance changes [2], chemicapacitors that detect changes in dielectric properties or polymer layer thickness [3-6], and mechanical oscillators that respond to mass changes [7,8]. Capacitive-type polymer based sensors can measure the response of a polymer film as a function of gas or vapor concentration and are the most preferable type of electrical sensors because of good response times, low-cost, low-power and relative ease of fabrication [3-6]. In such sensors, the polymer is used as a selective dielectric layer in a capacitor whose capacitance increases (decreases) as the analyte is absorbed into the polymer to change its permittivity (thickness).

The capacitive sensors have two geometries. The first geometry is based on Interdigitated Electrodes (IDE) [4, 5]. The sensor consists of two comb-shaped metal electrodes deposited on a substrate and a polymer deposited on top of them. The second type is a parallel-plate sensor that consists of a polymer layer sandwiched between two electrodes. The top electrode in the parallel-plate geometry must be porous for the analyte to reach to the sensing polymer. Etching voids in a top metal layer is challenging because metal etchants would destroy the polymer deposited under metal layer. One solution it is to create a parallel-plate MEMs structure with an etched porous electrode on top of the silicon wafer and then infiltrate the polymer later. This however requires sophisticated fabrication steps [3, 9]. The IDE based sensors are easier to make but they lack

sensitivity as most of the electric field lines pass through the substrate, while in parallel-plate sensor the lines pass through the polymer.

To overcome the existing difficulties in making parallel-plate geometry sensor structures [3, 9] we propose to use a nanoporous membrane material fabricated using standard silicon semiconductor processing techniques as an analyte-permeable electrode. The nanosmooth surface of the porous electrodes will also allow making ultrathin sensitive polymer layers to improve response and recovery times in the future.

Our sensor structure uses recently discovered porous nanocrystalline silicon (pnc-Si) membranes covered with metal to form capacitor plates while the polymer layer sandwiched between them serves as the sensing layer. Pnc-Si is new ultrathin (15 nm) membrane material [1] with pore sizes 5-50 nm and porosities up to 15 %. The pores in the material are formed spontaneously during rapid thermal annealing of an ultrathin a-Si layer sandwiched between two thin SiO₂ layers. These membranes have very good mechanical strength and flexibility, and are solvent and temperature stable. Here we present a study of pnc-Si membranes as a platform for capacitive sensing.

The polymer layer is spin-coated on the membrane and covers the pores. The pore openings then serve as nanometer diameter areas available for vapor adsorption. The degree of swelling and the reversibility of the polymer/pnc-Si membrane system immersed in analyte-containing vapors are observed using optical and electrical techniques. Preliminary results of the electrical response of the pnc-Si membrane based sensor to the polymer swelling and change of the dielectric constant in the presence of various analytes are discussed.

EXPERIMENTAL DETAILS

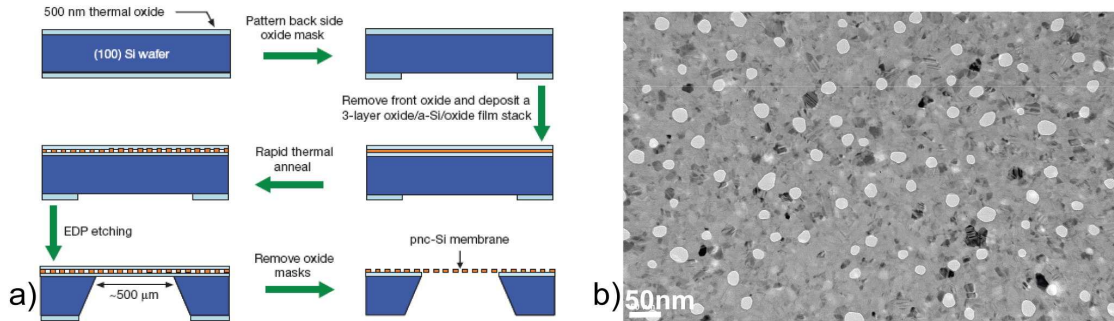


Figure 1. a) Pnc-Si membrane fabrication steps [1]; b) TEM image of a pnc-Si membrane where the white areas are the pores, the grey and black areas are silicon nanocrystals.

The pnc-Si membrane fabrication procedure is described in Fig.1a [1]. First, a thick SiO₂ layer thermally grown on both sides of a silicon wafer is patterned using standard photolithography to create a mask for membrane formation. Then the front oxide layer is removed and a three layer film stack (20 nm SiO₂/15 nm a-Si /20 nm SiO₂) is deposited on the front surface using RF magnetron sputtering. The structure is then treated at high temperature in a rapid thermal processing chamber. This treatment crystallizes the amorphous silicon film, forming a nanocrystalline film with voids that become the membrane pores. The patterned back side of the wafer is then etched with EDP (ethylenediamine pyrocatechol), which removes the silicon wafer along (111) crystal planes until it reaches the first SiO₂ layer of the film stack. Lastly, the three layer membrane is exposed to buffered oxide etchant (BOE) to remove the

protective oxide layers, leaving only the freely suspended ultrathin pnc-Si membrane. The membranes fabricated this way can have different dimensions, but the tests described in this paper were done on the chips that have a 3 x 3 array of 100 μm x 100 μm membranes.

A transmission electron microscopy (TEM) image of a pnc-Si membrane is shown in Fig.1b. The nearly circular white areas are the open pores in the membrane and the grey is the nanocrystalline silicon. The darker areas in the image are nanocrystals with crystal plane alignment satisfying the Bragg condition, so that electrons are diffracted and these nanocrystals appear black in this bright-field image.

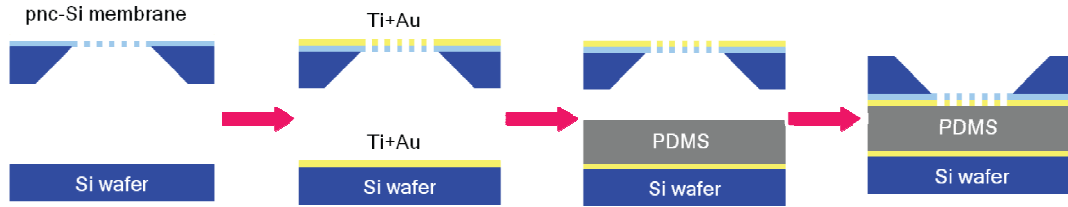


Figure 2. Hybrid pnc-Si membrane/PDMS/Si sensor fabrication steps.

The sensor fabrication process is illustrated in Fig.2. A 20 nm metal layer is first deposited on top of the pnc-Si membrane and on a silicon wafer chip using e-beam evaporation to create two electrode surfaces. This layer consists of a 10 nm of titanium adhesion layer under 10 nm of gold. The gold deposition on titanium is necessary because of the quick oxidation of the titanium layer. Titanium and gold are deposited in one run without breaking the vacuum. The next step is polymer deposition. In the preliminary experiments we chose to use polydimethylsiloxane (PDMS) Sylgard 184 from Dow Corning Corp. which is an easy to use and widely available polymer. The elastomer is first mixed with its curing agent in 10:1 ratio and then placed in a desiccator to remove the bubbles created while mixing. The PDMS layer is created by spin-coating pre-polymer on silicon at 6000 rpm for 3 min. The thickness of the resulted PDMS is approximately 10 μm based on the spin rate and duration. The pnc-Si chip and PDMS covered silicon chip are then bonded together and cured at 95°C for 2 hours.

DISCUSSION AND PRELIMINARY RESULTS

Membrane Metallization

After the metallization, the Ti/Au bilayer films on the pnc-Si membrane were imaged to ensure that pores have not been totally occluded. TEM images of the membrane without metal and with 20 nm of evaporated titanium and gold are shown in Fig. 3.

The pnc-Si membrane in Fig.3a has a distribution of pore sizes. Deposition of the metal layer on this pnc-Si membrane (Fig. 3b) covers all the smaller pores and decreases the size of the larger pores as metal coats the edges of the pores. However, the membrane is still porous and permeable after the metal coating and can be used as a conductive plate for a capacitive sensor. The porosity drops from 13-14 % to 3-4 % for membranes with an average pore diameter of 28 nm and from 4 % to < 1 % for membranes with an average pore diameter of 14 nm as measured by gas permeability experiments.

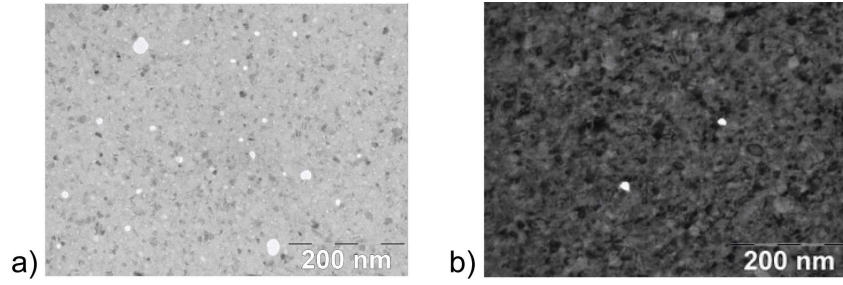


Figure 3. a) TEM of pnc-Si membrane with low porosity; b) TEM image of the same membrane with 10 nm of titanium and 10 nm gold coatings.

Optical Measurement of Vapor Permeation

The pore diameter in the pnc-Si membrane is approximately the same as the membrane thickness so the membrane overall exhibits negligible flow resistance. An experiment was conducted on the pnc-Si membrane/PDMS system to determine if the vapor above the pnc-Si membrane can permeate through pores, reach the polymer and induce changes in it. The goal was to measure the swelling of the PDMS induced by xylene vapor [10]. A structure consisting of a PDMS layer sandwiched between silicon and pnc-Si membrane chips was fabricated as the sensor structure described above in Fig. 2. It was then subjected to xylene vapor and the change in the surface height before and after the solvent introduction was measured.

Optical profilometry was used to measure the induced swelling of the Si/PDMS/pnc-Si structure. Optical profilometry is a white light interferometry technique. White light first passes through a beam splitter and is directed to the sample surface and a reference mirror. Reflected light from both surfaces is later recombined to produce interference fringe pattern which gives information about the surface contour of the sample. In this study a Veeco Wyko optical profiler was used.

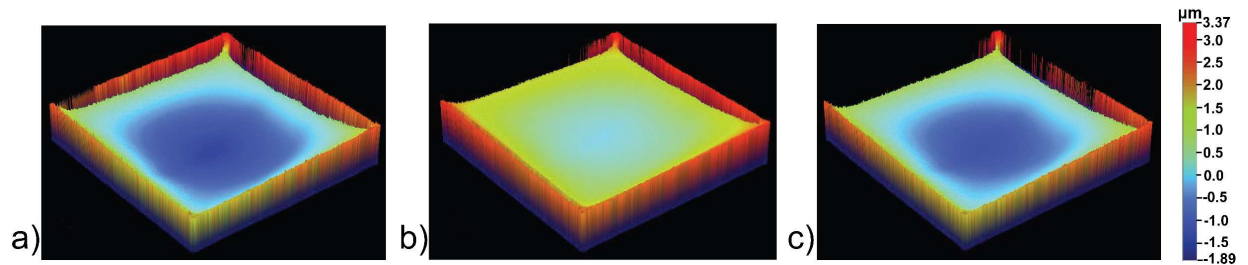


Figure 4. 3D optical profilometry images of a pnc-Si/PDMS/Si structure taken from the well-side of the pnc-Si membrane: a) initial structure before exposure to vapor; b) immediately after exposure to xylene vapor; c) approximately 2 minutes after the vapor is removed.

Fig. 4 shows 3D optical profilometry images of a pnc-Si/PDMS/Si structure taken from the well-side of pnc-Si membrane. The square window area in these images is the pnc-Si membrane covering PDMS layer. The surface height is represented by the color scale. The wall-like area around the membrane window is an artifact of the imaging as the optical profiler picks up the signal reflected not only from the square membrane area but also from the walls of the silicon well which was etched to expose the freestanding pnc-Si membrane. The deflection of the structure was observed before, during and after exposure to xylene vapor. Due to xylene vapor

permeation through the pores, PDMS swells and its thickness under the pnc-Si membrane increases. A 0.38 μm increase in thickness of the initial PDMS layer (Fig. 4a) under the membrane was measured when xylene vapor was introduced (Fig. 4b) into the system. After the vapor source was removed the membrane returned to its initial state as shown in Fig. 4c.

Capacitance Measurements of Vapor Permeation

To measure the capacitance of the complete sensor a computer was networked with a HP4275A multifrequency LCR meter controlled by Labview to collect real-time sensing data. All measurements were done in the parallel capacitive mode, with an AC signal of 10 kHz and voltage amplitude of 100 mV. The measurement setup is shown in Fig. 5a. Conductive silver epoxy was used to make wire connections to the sensor electrodes. The sensor chip was connected to the LCR meter with the backside well facing up to ensure vapor permeation through the porous membrane. Real-time data was collected during solvent introduction. A pipette was used to dispense small amounts of liquid solvents into the container where it evaporated. An immediate change in capacitance was observed. The sensor was then taken out to allow the capacitance to return to the baseline value, and then exposed to the solvent vapor again. This procedure was repeated several times.

The capacitance between plates of a parallel-plate capacitor is defined as $C = \epsilon_0 \epsilon_r A / d$, where ϵ_0 is the permittivity of vacuum, ϵ_r is the dielectric constant of the dielectric layer, A is the overlap area between two plates, d is the separation between plates. The effects of polymer swelling ($d + \Delta d$) and change of dielectric constant ($\epsilon_r + \Delta \epsilon_r$) may cancel each other. To maximize the capacitive response the polymer and solvent were chosen so that one of these mechanisms is dominant. Test solvents, including hexane, toluene, and acetone, were selected for this experiment as they are readily available, quick to evaporate and induce only one of two described above changes in PDMS. For hexane and toluene, polymer swelling dominates whereas for acetone vapor, dielectric constant change dominates.

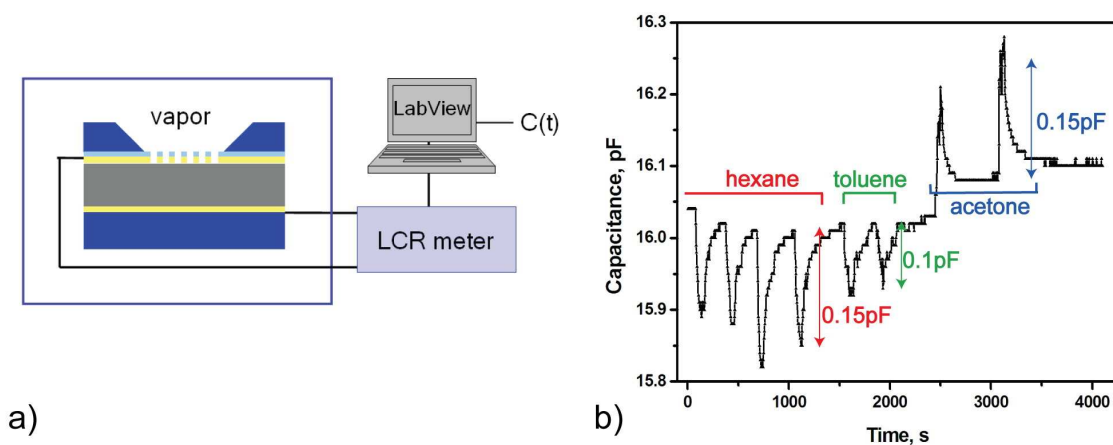


Figure 5. a) Capacitance measurement setup; b) real-time capacitance data with repetitive introduction of hexane, toluene and acetone vapor.

Preliminary experimental capacitance data is shown in Fig. 5b. First the sensor was repeatedly exposed to hexane and then toluene vapor of approximate concentrations of 800 ppm and 1000 ppm respectively. These solvents swell the PDMS, which increases plate separation

and decreases the capacitance. Hexane swells PDMS more than toluene, which is known from comparing their solubility parameters δ ($\delta_{\text{PDMS}} = \delta_{\text{hexane}}$ and $\delta_{\text{PDMS}} < \delta_{\text{toluene}}$) [10]. The dielectric constant of these two solvents is close to the dielectric constant of PDMS and the net change in dielectric constant is negligible. The changes in capacitance induced by hexane and toluene were 0.15 pF and 0.1 pF accordingly. Next the sensor was exposed to approximately 1200 ppm of acetone vapor. The dielectric constant of acetone ($\epsilon_{r \text{ acetone}} > \epsilon_{r \text{ PDMS}}$) is much higher than that of PDMS resulting in an increase of total sensor capacitance after acetone exposure. PDMS swelling by acetone is negligible [10]. The increase was measured to be 0.15 pF. The differences in capacitance values for the same vapor exposures occur because vapor concentrations were not precisely calibrated in these initial experiments and longer recovery times are needed to ensure that all the vapor diffuses out of the PDMS matrix.

CONCLUSIONS

A novel parallel-plate capacitive sensor that uses novel ultrathin pnc-Si membrane material covered with titanium and gold as an electrode was fabricated. The metal deposition is shown to keep the larger pores open and to allow the sensing analyte to permeate. The swelling caused by vapor permeation was measured by optical profilometry. Demonstration of real-time capacitance response of this sensor was presented for three solvents that induce two different mechanisms of capacitance changes, based on dielectric thickness or dielectric constant change. Future work will include fabrication of a flow-through capacitive sensor using two membranes as permeable plates. Since membrane and sensor fabrication is compatible with standard microfabrication processes there is significant potential for an entire detection system to ultimately be integrated on a single silicon chip.

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