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NANO FRACTURE CHEMICAL SENSOR FOR EXPLOSIVES DETECTION

Se Young Yang

Massachusetts Institute of Technology, Department of Mechanical Engineering
Cambridge, MA 02139, USA

Christy Petruczuk

Massachusetts Institute of Technology, Department of Chemical Engineering
Cambridge, MA 02139, USA

Hyungryul Johnny Choi

Massachusetts Institute of Technology, Department of Mechanical Engineering
Cambridge, MA 02139, USA

Ayse Asatekin

Massachusetts Institute of Technology, Department of Chemical Engineering
Cambridge, MA 02139, USA

George Barbastathis

Massachusetts Institute of Technology, Department of Mechanical Engineering
Cambridge, MA 02139, USA & Singapore-MIT Alliance for Research and Technology Centre (SMART), Singapore

Karen K Gleason

Massachusetts Institute of Technology, Department of Chemical Engineering
Cambridge, MA 02139, USA

ABSTRACT

Selective detection of explosive compounds is critical for national defense and homeland security. In this paper we describe the fabrication and demonstration of a chemical sensor capable of detecting nitroaromatic explosives in air. The device has the unique features of nano-scale dimensions, simple and inexpensive fabrication, and low power consumption. It consists of a nano-patterned conductive metal line placed on top of a patterned responsive polymer, poly(4-vinylpyridine) (P4VP). Due to polymer-solvent interactions, P4VP swells when it encounters the target analyte, producing a large stress. Detection takes place by monitoring the change in device resistance as the metal nano line deforms or fractures when P4VP swells and transfers mechanical stress.

The sensors would be ideal for discreet, wide-scale deployment over large areas. It is also important to note that device sensitivity can be readily enhanced by scaling down the feature size of the metal line or adjusting the material properties of both the metal and polymer. The fabrication process is readily transferrable to a variety of organic and metal materials, improving the versatility of the sensors. The resulting devices may provide new ways to detect security threats and complement existing complex methods to increase the probability of detection and to reduce false alarms. The same approach may also be applicable outside the military/security domain, for example, for pollution monitoring, for factory safety and operational monitoring, or for food quality

inspection; all these applications are contingent upon finding the appropriate polymers for the respective analytes.

INTRODUCTION

The ability to detect explosive compounds is a necessary attribute of forensic investigations, military actions, warzone remediation projects, and efforts to maintain transportation security [1]. Nitroaromatic compounds pose a particular threat; 2,4,6-trinitrotoluene (TNT), for example, is an inexpensive and readily available component of fifteen of the most widely used blends [2]. Existing methods to detect explosives include biosensors [3], electrochemical [4] and fiber optic [5] sensors, as well as devices utilizing chromatography [6] and Raman spectroscopy [7]. Sensors using the aforementioned techniques require complicated sensing and readout components; moreover, they are comparatively large in size and consume significant amounts of power during operation. The focus of this work is the development of a simple sensor that has unique

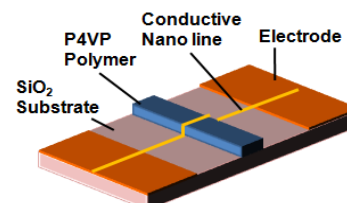


Figure 1. A schematic of the nano fracture chemical sensor

features of nano-scale dimensions, simple and inexpensive fabrication, and low power consumption. The sensor consists of a micro-scale P4VP line transected by a nano-scale metal line (Figure 1).

It is designed to utilize the swelling interaction between a nitroaromatic analyte and poly(4-vinylpyridine) (P4VP) to facilitate deformation and fracture in the nano patterned line. The appeal of the sensor is derived from its small footprint, low power consumption, and ease and cost of fabrication.

This paper demonstrates that the device sensitivity can be readily controlled and enhanced by scaling down the feature size of the metal line or adjusting the material properties of both the metal and polymer. Patterning of the polymer into nano and micro-scale lines has been achieved using electron beam lithography templates. A novel nano-scale pattern fabrication method is introduced using a nano-scale stencil mask and multi-angled e-beam evaporation. Wet processes are avoided so as to protect the P4VP lines from chemicals. The fabrication process is readily transferrable to a variety of organic and metal materials, and facilitates the mass-production of devices. The results indicate that ppm level exposure of nitroaromatic analyte results in a permanent increase in resistance; the change is large enough to be readily detectable.

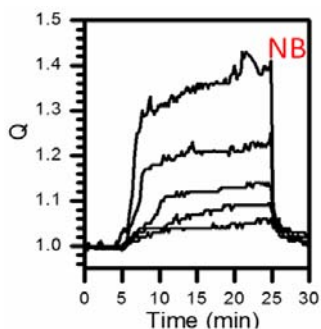


Figure 2. Swelling ratio (Q) of P4VP upon exposure to nitrobenzene at 40 °C for ppm values of 250, 490, 640, 740, 840 (Adapted from [12]).

CHARACTERIZATION AND DESIGN

P4VP is deposited using initiated chemical vapor deposition (iCVD). In contrast to high-energy CVD methods such as plasma-enhanced CVD (PECVD), iCVD is a low-energy process (0.02-0.12 W/cm²) that yields essentially 100% retention of functionality as well as excellent control over film thickness. The initiated chemical vapor deposition (iCVD) process provides a means of synthesizing functional and conformal polymer coatings, and is amenable to low-cost, large-scale production of nitroaromatic sensing devices with unique micro-scale geometries [8,9]. Figure 2 depicts the swelling response of iCVD P4VP upon exposure to increase in concentrations of nitrobenzene, a simulant of 2,4,6-trinitrotoluene (TNT). It shows the change in swelling ratio, Q (defined as the film thickness at time t divided by the original

film thickness) of P4VP by nitrobenzene at 40 °C for analyte concentrations of 250, 490, 640, 740, and 840 ppm. The swelling responses of P4VP films were measured via in situ interferometry. The increase and decrease in swelling ratio at 5 and 25 minutes correspond to the introduction and removal of analyte, respectively. The return of the swelling ratio to unity upon analyte removal indicates that the swelling response is fully reversible.

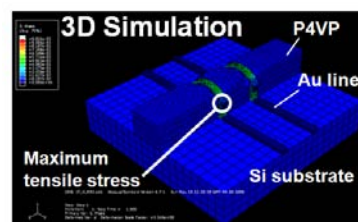


Figure 3. 3D linear finite element model.

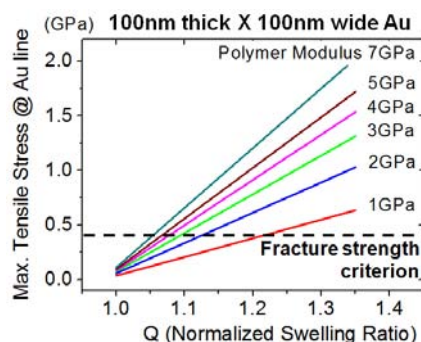


Figure 4. Change in maximum tensile stress at Au nano line with respect to material property (modulus) of P4VP.

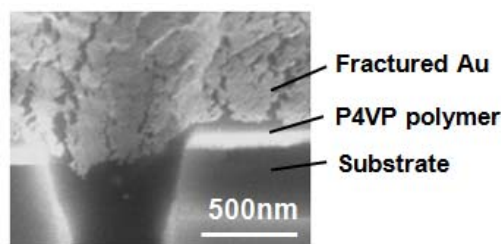


Figure 5. Fracture of an Au thin film in nano-thickness due to swelling of underlying P4VP thin film.

It is found that device sensitivity can be readily enhanced by scaling down the feature size of the metal line or adjusting the material properties of both the metal and polymer by 3D finite element calculations. Figure 3 illustrates the 3D finite element model used in this study. Pure elastic analysis using 8-noded, linear, and hexagonal meshes (C3D8R) with reduced integration was performed by ABAQUS CAE 6.7. The Mises

stress at the gold line was monitored and ultimate fracture stress for thin gold films from the work of Sharpe et al. [10] was used to define the failure. Maximum stress occurs at the upper corner of the vertical side wall of the line. Increasing the modulus of the P4VP increases the maximum stress at the side wall as shown in Figure 4. It is clearly revealed that high modulus P4VP will result in fracture of the line even with a low degree of swelling. Nanoindentation measurements on P4VP yield a Young's modulus of 6.4 GPa, a value in agreement with a glassy polymer. Increasing the modulus of P4VP can be readily achieved by changing the degree of cross-linking of the polymer. Figure 5 shows an SEM image of a thin Au film in fractured due to swelling of an underlying P4VP layer. Figure 6 illustrates that the stress at the line can be further increased by decreasing its dimension. The line becomes significantly easier to fracture below a thickness of 100nm.

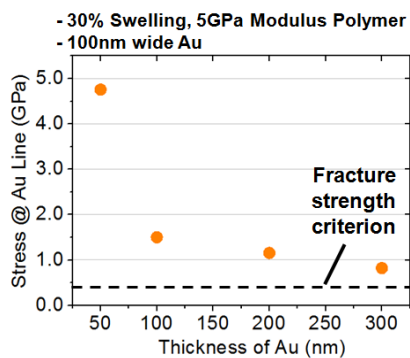


Figure 6. Change in maximum tensile stress at Au nano line with respect to change in its dimension

DEVICE FABRICATION

The fabrication process for the device is shown schematically in Figure 7. Device electrodes were fabricated using photolithography. A silicon wafer (4-inch, 100 nm SiO₂ layer) was coated with 10nm of Cr by e-beam evaporation, then spin-coated with 1.5 μ m of S1813 photoresist (Shipley). A 4-inch transparent mask was applied and the wafer was exposed for 10 s using a Tamarack Scientific ultraviolet stepper (λ =400 nm, 20 mW/cm²). The photoresist was developed in room temperature with MF-321 for 1 min. Remained photoresist patterns were then used as etch mask, as the wafer was soaked into Cr etchant (CR-7) to form Cr electrodes. The remaining S1813 patterns were removed by rinsing the wafer with acetone for 5 min followed by a 1min IPA rinse.

Polymer line templates of varying widths (500 nm-10 μ m) were obtained by exposing PMMA resist (160 - 200 nm) with a Raith 150 electron-beam lithography system (10 keV, 110 μ As/cm²). After exposure, the films were developed in a 2:1 isopropyl alcohol (IPA): methyl isobutyl ketone (MIBK) mixture for 60 s, followed by a 60 s IPA rinse. Deposition of P4VP films onto the PMMA templates was achieved using an iCVD reactor described in [11] and method explained in [1].

Removal of the PMMA template and subsequent isolation of the P4VP line was achieved by a lift-off process soaking the coated template in room temperature toluene for 1.5 h with 15 s of ultrasonication treatment every 15 min. Figure 8 depicts the high selectivity achieved between the PMMA and P4VP.

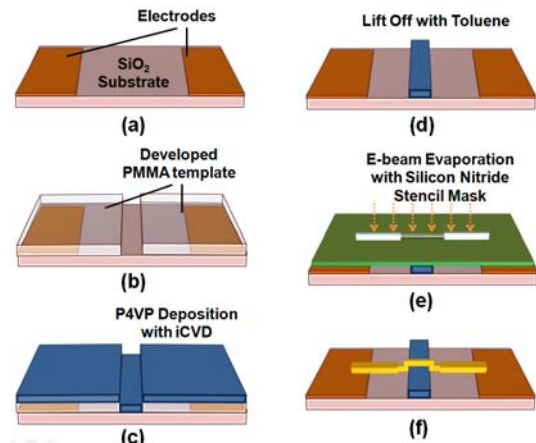


Figure 7. Schematic of the fabrication process

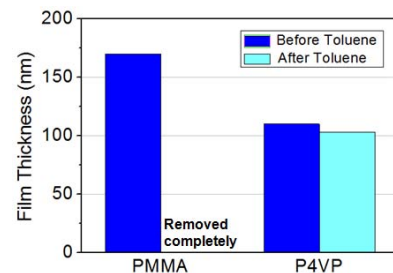


Figure 8. Thicknesses of PMMA template and P4VP before and after toluene lift-off treatment.

Fabrication of the shadow masks for gold patterning was achieved by KOH-etching a wafer coated with LPCVD silicon nitride. 10 nm of Cr were electron beam-evaporated onto the wafer, followed by a 160 nm layer of spin-coated PMMA resist. The mask pattern was exposed and developed using the e-beam lithography and developing procedures described above. The pattern was transferred to the Cr using CR-7 etchant, with the undeveloped PMMA acting as an etch mask. Transfer to the silicon nitride membrane was achieved using CF₄ reactive ion etching. Masks with line widths ranging from 100-300 nm were defined.

Patterning of a transverse gold line was accomplished using multi-angled electron beam evaporation through the silicon nitride shadow mask. 100 nm of gold was deposited at incident angles of -30°, 0°, and +30° from the normal to enhance the conformality of the coating. Silver epoxy was used to attach wire leads to the electrodes for measuring device resistance.

EXPERIMENTAL RESULT

Electrodes, P4VP lines, nano shadow masks, and transecting Au lines of various dimensions have been successfully fabricated. Figure 9 shows SEM image of a fabricated, 1 μm wide P4VP line. The fabricated nano shadow

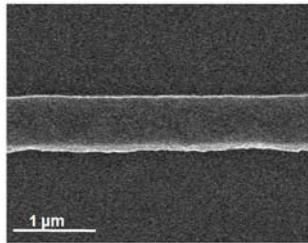


Figure 9. SEM image of a fabricated P4VP line

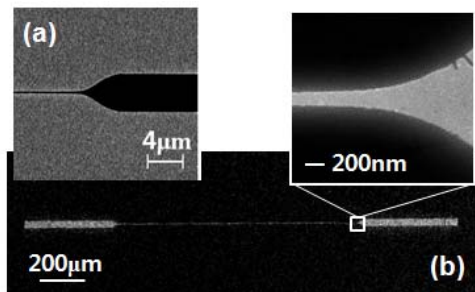


Figure 10. SEM image of (a) fabricated silicon nitride nano shadow mask and (b) e-beam evaporated Au line on bare silicon using the mask for validation.

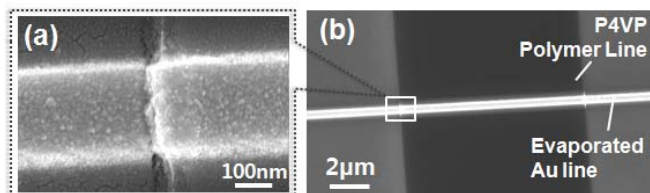


Figure 11. SEM image of fabricated intersected line device: (a) Magnified view at the side wall; (b) Overall view.

mask for nano Au line patterning is shown in Figure 10. Metal lines with a 50 nm pattern width can be readily achieved by this approach. Figure 10(a) shows the fabricated 500 nm-thick silicon nitride shadow mask with a 100 nm line width opening. The mask was used to deposit Au nano lines via e-beam evaporation on a bare silicon substrate for verification (Figure 10(b)).

In order to avoid further wet process so as to protect the P4VP lines from chemicals, metal lines were e-beam evaporated using a nano-scale shadow mask. Figure 11 illustrates a completed device with 10 μm wide P4VP line intersected by 300nm wide, 60nm thick Au line. Conformality

of the Au down the side walls of the device was confirmed via SEM (Figure 11(a)) and by measuring the initial resistances across the devices. These values, which are on the order of 0.1-1 M Ω (depending on the thickness of the evaporated Au), correspond well with the calculated resistance of wires with rectangular cross sections and these dimensions.

Fabricated devices were tested for their response to nitroaromatic exposure using a previously described system [12,13]. Test devices were located on a cooled stage within a flow cell; swelling responses of P4VP films were measured via in situ interferometry. The device resistance was monitored using a multimeter connected to the device electrodes using a conductive wire and conductive Ag epoxy. Figure 12 illustrates the change in device resistance for a 200 nm-thick, 5 μm -wide P4VP line intersected by 100nm-thick, 300nm-wide Au line sensor upon exposure to 500 ppm of nitrobenzene. The concentration was increased to 650 ppm at $t=15\text{mins}$. The change in resistance corresponds well to the change in exposure concentration. A permanent increase (8.5%) in resistance is clearly observed as the result of permanent deformation and micro-cracks; this change is large enough to be easily detected.

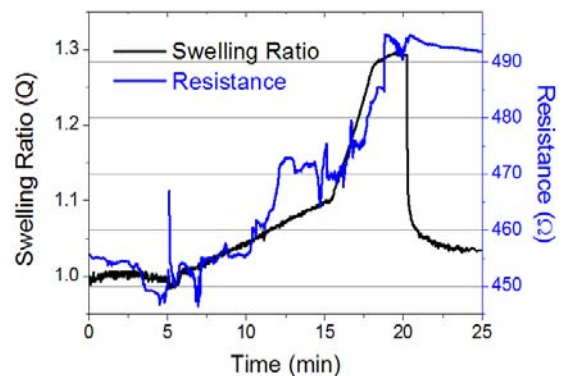


Figure 12. Change in device resistance of a 100nm-thick, 300nm-wide Au line sensor upon exposure to 500 ppm of nitrobenzene. The concentration was increased to 650 ppm at $t=15\text{mins}$.

SUMMARY

Successful design and fabrication of the nano fracture sensor have been demonstrated in this work. The responsive iCVD polymer, P4VP, exhibits a notable swelling response when exposed to ppm levels of nitroaromatic analyte. Electron beam lithography and a lift-off process were used to pattern the polymer into nano- and micro-scale lines. A novel method of fabricating nano-scale shadow masks was introduced; these masks were used to pattern an intersected nano-scale Au line on the P4VP line. This method avoids further wet processes and allows the functionality of the P4VP to be retained. The entire fabrication process is readily transferrable to a variety of organic and metal materials, and facilitates the mass-production of single-use, disposable devices. The change in device

resistance upon exposure to a ppm level of nitrobenzene (acting as stimulant to TNT) successfully demonstrates the detection of nitroaromatic explosive compounds in air. It has been shown theoretically that further enhancement in sensitivity can be achieved by scaling down the dimension of the Au lines or by increasing the modulus of the P4VP. The developed sensor has the unique features of nano-scale dimensions, simple and inexpensive fabrication, and low power consumption. The device is ideal for disposable one time sensing and wide-scale deployment over large areas.

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