



# An ultra-sensitive piezoresistive polymer nano-composite microcantilever sensor electronic nose platform for explosive vapor detection



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## ABSTRACT

In the present paper, we demonstrate a compact, nonoptical, and inexpensive polymer nano-composite microcantilever sensor platform for the detection of 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-triazine (RDX) and pentaerythritol tetranitrate (PETN) vapors at room temperature. In order to achieve sufficient selectivity, the piezoresistive polymer nano-composite microcantilevers coated with gold surfaces are modified with self-assembled monolayers (SAM) of 4-mercaptobenzoic acid (4-MBA), 6-mercaptonicotonic acid (6-MNA) and 2-mercaptonicotonic acid (2-MNA). The SAMs formation is confirmed by FTIR and contact angle measurements. The ultrahigh sensitive piezoresistive polymer nano-composite microcantilever provides detection sensitivities in the below parts-per-trillion level within few seconds of exposure under ambient conditions. Maximum bending of the microcantilever is achieved within 20 s with response and recovery time of ~3 s and 4 s, respectively. The cross selectivity of 4-MBA and 6-MNA coated microcantilevers is confirmed by investigating exposure to different organic compounds. We also demonstrate that the polymer nano-composite microcantilever is ideally suited for “electronic nose” applications. Further, the ultra-high sensitivity and low cost of polymer nano-composite microcantilever can lead to the development of a rugged portable, handheld device for rapid and sensitive detection of explosive vapors.

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## 1. Introduction

Rapid detection of explosives and similar substances is very important concerning the homeland security and environmental safety requirements. Current detection methods typically include mass and ion mobility mass spectrometers that can identify the constituents of complex mixtures of analytes [1–4]. However, such diagnosis methods involve large, expensive, sophisticated instruments and are time consuming. The demands of the 21st century (e.g., the war on terrorism, landmine detection, etc.) dictate a need for miniaturized and inexpensive sensors. Miniature gravimetric sensors such as surface acoustic wave (SAW) sensors [5,6] and quartz crystal microbalance (QCM) sensors [7] are not small enough to be incorporated in large numbers in an array (necessary to achieve selectivity) configuration. Besides, these sensors also require frequency-measuring equipments that are large and expensive.

Accordingly, portable sensors that can detect gaseous molecules at concentrations as low as parts per billion (ppb) or even

parts per trillion (ppt) are in great demand. Among a variety of trace-level-detecting sensors that are under development, microcantilevers modified with sensitive molecular layers have attracted much attention as they offer the advantages of smaller size, low power consumption, extremely high sensitivity attributed to the associated high surface area to volume ratio and versatility to integrate multiple explosive detectors in a single miniature package [8–13]. The change in the Gibbs surface free energy is induced by surface-analyte interactions lead to differential stress thereby causing the microcantilever to bend [14]. Microcantilever based sensors have been demonstrated to detect trace-level explosive vapors such as 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-triazine(RDX) and pentaerythritol tetranitrate (PETN). As reported in the literature a ppt level of analytes have been detected within seconds using the optical detection system based on microcantilever bending. This involves measurement of change in displacement or resonance frequency using a laser beam bouncing off the microcantilever tip. [15,16]. Such diagnosis method involves large, expensive, sophisticated instruments and moreover, the detection system is not suitable for a rugged and easy-to-use portable sensor.

The piezoresistive microcantilever readout method has also been demonstrated to result in an ultra-sensitive detection of

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trace-level vapors [10,13,14,17,18]. The specific molecular adsorption on a cantilever surface significantly changes the surface stress thereby leading to a change in the resistance of the piezoresistive layer. The surface stress sensitivity depends on the ratio of the gauge factor ( $K$ ) of the piezoresistive film to Young's modulus ( $E$ ) of the structural material.

The conventional microcantilevers are normally made of Si/SiO<sub>2</sub> which has a high Young's modulus and are sensitive for static deflection measurements. Recently, polymer with a much lower Young's modulus than that of silicon such as SU-8 ( $E$ , ~40 times smaller compared to silicon) are demonstrated and considered for structural layers. SU-8 microcantilevers with various strain sensitive layers like gold (Au) [19] and polysilicon have been reported earlier. Gold is less sensitive due to the lower gauge factor. Low temperature deposited polysilicon film should be sufficiently thin enough to avoid any contribution to the stiffness of the structure and decreased signal to noise ratio [20]. The limitations of using piezoresistive materials can be overcome by integrating polymer nano-composite as the strain sensitive layer. Subsequently, Gammelgaard et al. [21] reported SU-8 microcantilever integrated with SU-8/carbon black (CB) polymer composite having a gauge factor in the range of 15–20. We have recently demonstrated polymer nano-composite microcantilever for TNT detection. The improved performance was achieved by controlling the dispersion parameters of CB in SU-8 [13,22].

In the present work, we report SU-8 nano-composite microcantilevers equipped with gold surfaces modified with three different self-assembled monolayers of 4-mercaptopbenzoic acid (4-MBA), 6-mercaptopnicotonic acid (6-MNA) and 2-mercaptopnicotonic acid (2-MNA) to achieve better selectivity for the trace level detection of explosives such as TNT, RDX and PETN. Further, we demonstrate that the detection sensitivities at levels below ppt (parts per trillion) can be achieved within a few seconds of exposure under ambient conditions. The ultra-high sensitivity and low cost can lead to the development of a rugged portable, handheld device for rapid and sensitive detection of explosive vapors. We envision this sensor platform to eventually incorporate few tens of microcantilevers functionalized with different receptor layers in a single chip with wireless networking in order to achieve simultaneous detection of a wide variety of analytes with low false alarm rates.

## 2. Experimental details

### 2.1. Materials and chemicals

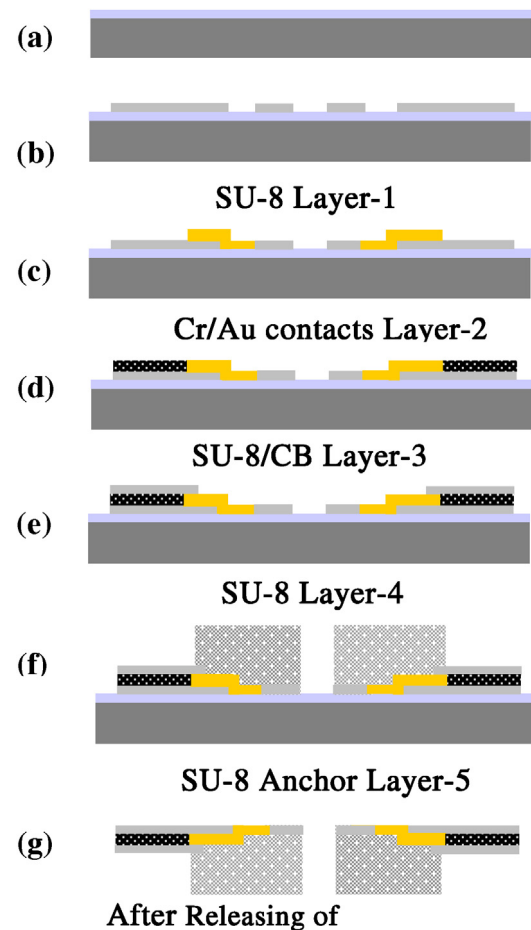
Carbon black (CB) Conductex 7067 Ultra from Columbian Chemicals, USA. SU-8 a transparent negative-tone epoxy based photoresist (2002-2100) and nano-thinner was purchased from MicroChem, MI, USA. 4-Mercaptobenzoic acid (4-MBA), 6-mercaptopnicotonic acid (6-MNA) and 2-mercaptopnicotonic acid (2-MNA) were purchased from Sigma-Aldrich (St. Louis, MO, USA).

### 2.2. Measurement techniques

Contact angle meter, CAM-100, KSB, Finland was used to identify the wettability of the self-assembled monolayers. Perkin Elmer's FTIR Spectrum-100 was used to identify the functional groups/bonds on the self-assembled monolayers. Raith 150<sup>two</sup> SEM was used for microcantilever imaging.

### 2.3. Microcantilever fabrication

The polymer nanocomposite microcantilevers for the trace detection of explosives such as TNT, RDX and PETN were fabricated



**Fig. 1.** Fabrication process sequence for polymer nano-composite microcantilevers. (a) Silicon dioxide as a sacrificial layer, (b) first layer of SU-8, (c) Cr/Au for contacts, (d) SU-8/CB composite layer, (e) encapsulating SU-8, (f) thick SU-8 die base and (g) release of cantilever die from the substrate.

using the process as described earlier [13,23]. Microcantilevers having length, width, and thickness of 250  $\mu\text{m}$ , 100  $\mu\text{m}$ , and ~3.5  $\mu\text{m}$ , respectively, were used. The nanocomposite polymer microcantilever fabrication process sequence is illustrated in Fig. 1. The fabrication starts with RCA cleaning of silicon substrate. The term RCA stands for 'Radio Corporation of America' which refers to the standard set of wafer cleaning steps that involves three basic steps, i.e. removal of organic contaminants, oxide strip and the ionic clean. This is achieved by first cleaning the wafer in a 1:1:5 solution of NH<sub>4</sub>OH (ammonium hydroxide, 27%) + H<sub>2</sub>O<sub>2</sub> (hydrogen peroxide, 30%) + H<sub>2</sub>O (water) at 75 or 80 °C typically for 10 min followed by immersion in a 1:50 solution of HF + H<sub>2</sub>O at 25 °C and subsequent dipping in a 1:1:6 solution of HCl + H<sub>2</sub>O<sub>2</sub> + H<sub>2</sub>O at 75 or 80 °C. Thermally grown silicon dioxide of thickness ~500 nm was used as a sacrificial layer. SU-8 structural layer (SU-8 2000.5, Microchem, MI) was spin coated and pre-exposure baked for optimized timings with a slow ramp up and ramp down to room temperature. To transfer the microcantilever pattern (Layer-1, Fig. 1(b)), samples were exposed to UV light using Karl Suss MJB-3 mask aligner and subjected to a post exposure bake cycle, development and rinsing with iso propyl alcohol (IPA). A thin layer of Cr/Au (10 nm/200 nm) was deposited by sputtering, and the contact pads were patterned using positive photo resist (PPR) photolithography with the corresponding mask (Layer-2, Fig. 1(c)). The Cr–Au layer was wet etched in respective etchants. To obtain an electrically conductive and a piezoresistive layer, SU-8/CB nano-composite was prepared by dispersing CB 8–9 vol.% in SU-8. The nano-composite was spin coated

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