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Integration of Reactive Polymeric Nanofilms Into a Low-Power Electromechanical Switch for Selective Chemical Sensing

William J. Arora, Member, IEEE, Wyatt E. Tenhaeff, Karen K. Gleason, and George Barbastathis, Member, IEEE

Abstract—This paper presents the fabrication and demonstration of an ultrathin microelectromechanical chemical sensing device. Microcantilevers are etched from 100-nm-thick silicon nitride, and a 75-nm-thick reactive copolymer film for sensing is deposited by initiated chemical vapor deposition. Cross-linking densities of the polymer films are controlled during the deposition process; it is shown that greater cross-linking densities yield greater cantilever deflections upon the polymer’s reaction with the analyte. Considering that chemical reactions are necessary for stress formation, the sensing is selective. Cantilever deflections of greater than 3 μm are easily attained, which allow a simple switch to be designed with resistance-based outputs. When exposed to a hexylamine vapor-phase concentration of 0.87 mol%, the resistance of the switch drops by over six orders of magnitude with a response time of less than 90 s.

Index Terms—Chemical–vapor deposition (CVD), microsensors, thin films, three-dimensional nanomanufacturing.

I. INTRODUCTION

C

HEMICAL-SENSING science is a field with many applications in industries, security, and defense. A multitude of detection mechanisms exists but many are only applicable to very specific situations. Generally, effective chemical sensing needs to be highly selective to a target analyte and result in a large electrical response. Here, we demonstrate a sensing mechanism that achieves high selectivity because it relies on covalent bond formation and achieves a large electrical resistance change due to its design as an electromechanical switch. The chemically selective component is a reactive polymer deposited by initiated chemical–vapor deposition (iCVD) [1] onto a 3-D microswitch. The polymer is engineered to produce a large stress when it reacts with the analyte, deforming the switch and causing it to short-circuit. We present a nonoptimized proof-of-concept device that uses a maleic anhydride copolymer thin film to detect amines. Before reacting with hexylamine, the device is an open circuit (drawing negligible power), and after the reaction, the resistance drops by over six orders of magnitude. Although this first fabricated prototype has sensitivity limits in the parts per thousand range, achievable geometric modifications will be discussed that are predicted to improve detection down into the parts per billion (ppb) range. In addition, it is anticipated that a wide range of analytes can be detected by using the general platform method of iCVD to synthesize additional types of reactive organic nanocoatings, each offering a specific complimentary reactive functional group [2], [3].

Transducing a chemical response into an electrical response can be done most directly with a chemiresistive polymer, in which the reaction either acts to dope or undope a semiconducting polymer [2] or cause a conductivity change by swelling a partially conductive polymer [3]. However, these methods suffer from lack of analyte specificity, offer small resistance changes, and draw continuous power. Instead, an intermediate transduction step, often optical or mechanical, is used. Microcantilevers are a common platform for transducing the chemical response into a mechanical one. One surface of the cantilever is coated with a material (often a polymer) that the target chemical will interact with, typically through absorption (swelling) or reaction.

The interaction creates a stress that causes the cantilever to bend. Existing methods rely on measuring small cantilever deflections of less than a few micrometers [4] or measuring resonance frequency changes due to a mass increase. In order to measure these small changes, optical [5], piezoelectric [6], piezoresistive [7], or capacitive [8] schemes are employed. These measurements are susceptible to ambient interference and require additional power-consuming electronic circuitry. It has been suggested that the requirement of relatively thick sensing layers, typically on the order of several micrometers, in soft-matter-based sensors (i.e., polymers) is another major disadvantage as it limits their incorporation into nanoscale devices [9]. The best cases of “ultrathin” sensors have thicknesses greater than 300 nm. Furthermore, such systems show only partial selectivity, which is based on the rate of different molecules diffusing into polymer layers. Herein, we report the sensing of analytes based on chemical reactions in the polymer where the polymer sensing layer is 75 nm thick.
II. Design

Our sensing concept produces large cantilever deflections because it uses a polymer capable of generating stresses of greater magnitude and because the cantilever is very thin (100 nm). The large deflection allows the cantilever to act as a switch. The assembly and operation of this switch are shown in Fig. 1, and fabrication details are described in Section III. Our work on the Nanostructured Origami method of folding patterned membranes into 3-D microstructures [10]–[12] inspired the 3-D architecture of the switch. Previously, we used the stress from a deposited metal or ion implantation to controllably fold a thin silicon nitride cantilever into a static structure. Here, the structure is dynamic because the cantilever bends as the polymer stresses. Initially, the switch is an open circuit [Fig. 1(b)] separating a battery from circuitry such as an RF transmitter. Therefore, almost no power is consumed until the switch closes, and no logic circuitry is needed to determine a threshold of cantilever deflection magnitude.

In addition to an improved transduction scheme, sensing selectivity is improved by using another recently developed technique, iCVD [1]. iCVD enables the design of the deposited polymer with specific functional groups that will chemically react with the target analyte. Several choices of functional monomers are available, meaning that many classes of compounds can be sensed. In this paper, we use maleic anhydride (Ma) because we were familiar with its properties from previous studies [13]. The reactivity of the anhydride functionality enables the detection of amines; hexylamine is used as a model analyte in this paper. Detection of amines is important for industrial and environmental monitoring, food quality control, and diagnosis of certain diseases [14]. Low concentrations of aliphatic and aromatic amines can cause toxicological responses [15].

Maximizing the bending force and deflection magnitude of the polymer-coated cantilevers is critical for minimizing the response time and contact resistance of the closed switch. For effective transmission of the stress into mechanical bending, there must be good adhesion at the polymer–cantilever interface to ensure effective transmission of the stress into mechanical bending, and therefore the magnitude of the strain should increase with the increasing analyte size. To analyze the effect of analyte volume on stress, we make the assumption that there is a limiting value for \( v_{ex} \) due to the presence of cross links, while \( v_{sf} \) will increase concomitantly with analyte size in order to maintain a constant density. Therefore, the magnitude of the strain should increase with the increasing analyte size.

III. Experimental Procedures

A. Device Fabrication

Silicon nitride membranes windows (1 \( \times \) 1 mm, 100 nm thick) are formed by backside tetramethyl ammonium hydroxide etching of silicon. Photoresist is spun directly onto the membrane, exposed with cantilever shapes using a contact mask, and developed. The membrane is etched with a CF\(_4\) reactive ion etch (100 V, 200 W, 10 mtorr) until the cantilever border is completely etched. The sample is cleaned in an oxygen plasma (200 W, 400 mtorr) which removes the photoresist. The frontside is coated with electron-beam-evaporated titanium (3 nm, for adhesion) and gold (5 nm). To ensure good adhesion between the subsequent polymer deposition and the silicon nitride, the cantilevers are primed with a monolayer of 3-aminopropyl(dimethylthioxysilane in a vapor chamber at 60 °C. The sample is placed gold side down into a reaction chamber for iCVD polymer deposition so that the underside (nongold side) of the cantilever is coated with polymer. Although the membrane and free-standing cantilevers are placed directly onto the aluminum chamber stage, they do not break. One of the advantages of iCVD over traditional CVD is that the conformality of the polymer coverage can be adjusted by controlling the surface concentrations of the monomers and initiator [18]. In this case, we use a low initiator flow rate and high monomer surface concentrations to make the coverage nonconformal and avoid coating the gold side. Furthermore, we have found that this principle permits us to lithographically pattern the deposited polymer using shadow masking or liftoff, both done directly on a free-standing cantilever. These negative tone-patterning processes allow adjacent cantilevers on the same chip to be coated with different polymers, for multiplexed sensing.

On a separate substrate, a set of interdigitated gold wires is patterned to form an open circuit (as shown in Fig. 1). The space around the wires is covered with a 3-\( \mu \)m thick polymer that is patterned by photolithography. Finally, the device is assembled by placing the cantilever gold side down above the wires so that a \( \sim 3-\mu \)m gap is maintained by the spacer polymer.

B. Polymer Film Synthesis

Poly[maleic anhydride-co-vinyl pyrrolidone-co-di(ethylene glycol) di(vinyl ether)] [poly(Ma-V-D)] is synthesized by...
flowing maleic anhydride, vinyl pyrrolidone, and di(ethylene glycol) di(vinyl ether) (Dedve) monomers into a previously described iCVD chamber [13] at rates of 3.6, 1.3, 0.5 sccm, respectively. Poly[maleic anhydride-alt-di(ethylene glycol) di(vinyl ether)] [poly(Ma-D)] is synthesized by feeding maleic anhydride and Dedve at 3.6 and 1.2 sccm, respectively; an alternating copolymer is formed because neither monomer will undergo free-radical homopolymerization to a significant extent [13], [19]. In both polymer depositions, 0.4 sccm of tert-butyl anhydride and 4 sccm of Ar diluent flow are introduced. The filament temperature is 235 °C; the substrate temperature is 25 °C, and the chamber pressure is 250 mtorr. X-ray photoelectron spectroscopy using a monochromatized Al Kα source (Kratos Axis Ultra) revealed that poly(Ma-V-D) is 53.4% maleic anhydride, 35.7% vinyl pyrrolidone, and 10.9% Dedve, while poly(Ma-D) is 60.5% maleic anhydride and 39.5% Dedve. During the deposition, film thickness is controlled and measured by in situ laser interferometry on polished silicon wafer monitors.

C. Device Testing

The sensors were tested in a vapor chamber constructed from an aluminum block with a cavity for vapor introduction; the block was bolted to a temperature-controlled stage on which the device was placed. The stage was maintained at 40 °C. Nitrogen flow rates into the chamber were controlled with mass flow controllers (MKS Instruments, Model 1479). One nitrogen line (ultrahigh purity, Airgas) was bubbled through the liquid analyte, where it became saturated with the analyte vapor. The second line of nitrogen was mixed with the saturated analyte stream prior to entering the chamber to control analyte concentrations. Electrical resistances were logged with a multimeter (Agilent, U1252A) attached to the sensors’ electrical leads.

Before and after the reaction with hexylamine, Fourier transform infrared spectroscopy (FTIR) spectra of blanket polymer films on Si were collected (Nicolet, Nexus 870). Sixty-four scans, from 500 to 4000 cm⁻¹ with a 4-cm⁻¹ resolution, were collected and integrated using a deuterated triglycine sulfate KBr detector. The bare Si wafers served as backgrounds. Thicknesses were determined using spectroscopic ellipsometry, with an incident angle of 70° and 190 wavelengths between 315 and 718 nm (J. A. Woollam, M-2000).

IV. RESULTS AND DISCUSSION

We compare two polymers, namely, poly(Ma-V-D) and poly(Ma-D). Fig. 2 shows images of cantilevers coated with these two polymers before and after the reaction with hexylamine. There is little observable additional deflection of the cantilevers coated with poly(Ma-V-D) due to the hexylamine reaction, since most of the stress from the added volume of hexylamine is relieved through expansion. This degree of expansion is much more limited in the more cross-linked poly(Ma-D) film resulting in the accumulation of stress desired for deflecting the cantilever. However, the cross-linking in poly(Ma-D) also reduces the diffusion of the analyte, creating a tradeoff between stress accumulation and extent of reaction as the degree of cross linking varies. In making the prototype device, we did not optimize the degree of cross-linking and used the poly(Ma-D) polymer comprised of 39.5% cross-linker, as shown in Fig. 2(d)–(f). Although there is a significant initial curvature with the poly(Ma-V-D) coatings, 75-nm-thick poly(Ma-D) films, which were used for device fabrication, resulted in negligible curvature before the hexylamine reaction. Assuming that the reaction goes to completion and the polymer layer is uniformly elastically stressed, the cantilever curvature k can be calculated analytically [10] as

\[
k = \frac{6E_1E_2t_1t_2(t_1 + t_2) \cdot (\sigma/E_2)}{E_1^2t_1^2 + E_2^2t_2^2 + 2E_1E_2t_1t_2 \cdot (2t_1^2 + 2t_2^2 + 3t_1t_2)}. \tag{2}
\]

The material parameters for this experiment are as follows. Plate modulus $E_1 = 300$ GPa for silicon nitride; $E_2 = 5$ GPa.
Comparison of stress formation in lightly and highly cross-linked maleic anydride polymers after reacting with hexylamine. Silicon nitride cantilevers, with 100-nm thickness, are coated with iCVD polymer on their undersides. Compressive stress within the polymer causes the cantilevers to bend upwards; the amount of stress determines the curvature. In (b), the cantilevers are initially bent due to intrinsic stress within the polymer from deposition, whereas in (e), there is very little initial stress in the polymer (desired). In both cases, the hexylamine reaction lasted for 60 min, at a concentration of 0.87% in atmosphere, at 40 °C.

The poly(Ma-V-D) expanded by 102% and stressed minimally while the poly(Ma-D) expanded by 32% and stressed significantly, as evidenced by the increased curvature. In addition, FTIR measurements revealed that 95% of the maleic anhydride had reacted in the poly(Ma-V-D) sample versus only 49% in the poly(Ma-D) sample, indicating how severely increased cross-linking lowers the diffusion rate.

For these parameters, a polymer thickness between 200 and 300 nm produces a near-maximized curvature. In our experiment, we used a 75-nm-thick polymer layer. Based on results shown in Fig. 2, we deduced that the reaction was diffusion limited and that only the top region of the nanocoating reacted with the analyte in our devices.

We fabricated a prototype switch to demonstrate the concept. Images of the assembled switch, both before and after reacting with hexylamine, are shown in Fig. 3.

Device performance was assessed by measuring the electrical resistance of the wire leads as hexylamine was introduced to a gas chamber. Resistance versus time plots are shown in Fig. 4 for four different hexylamine concentrations. In all cases, the electrical response exhibits a drop of several orders of magnitude as one would expect from a contact switch. The response time $\tau$ of the sensor is inversely proportional to the gas concentration and, given the data in Fig. 4, fits to a power law of $\tau = 0.004 \cdot X^{-1.3}$, where $X$ is the hexylamine concentration.

At nine parts per thousand of hexylamine in nitrogen, the response time is under 2 min and increases to about 700 min for a concentration of 90 parts per million (ppm). Devices were also tested for selectivity to hexylamine by exposure to nitrogen streams saturated with heptane, 2-propanol, and water. The resistance did not drop over each 12-h test. Considering that chemical reactions are responsible for creating stress, the device is insensitive to chemicals that do not react with maleic anhydride. However, the device should be sensitive to other amines, alcohols, and nucleophiles that will react with maleic anhydride. Although 2-propanol, which was used as a control, is an alcohol, it does not react with maleic anhydride [20]. To discriminate between analytes in a given class of chemical compounds, an array of cantilevers with varying aspect ratios can be coated. Analytes with large volumes will create enough stress to deflect all of the cantilevers, while the small analytes would create only enough stress to deflect the longest cantilevers. To discriminate between classes of chemicals, multiple polymers with differing functionalities can be deposited.

After reacting the devices with hexylamine, we exposed them to 100% nitrogen for 24 h and observed that the resistance remained constant, indicating that the cantilevers remained stressed and bent. The tradeoff of attaining high selectivity by chemical binding is that each switch can only be used once and
must be replaced afterward. However, in return, we derive great benefit from the low manufacturing cost of each switch.

The response times in our present experiments are slow for most applications but can be improved by optimizing the cantilever geometry to make it more compliant. Given a cantilever that is required to bend with curvature of length \( l \), the resistance and \( h \) above the electrode wires, it is required to bend with curvature \( k \), where \( k = h/l^2 \), in order to short-circuit the electrode wires (to arrive at this expression, we assume that \( \cos(2k) \approx 1 - (2k)^2 \) because the curvature is small when \( h \ll l \)). Therefore, increasing the length of the cantilever reduces the required curvature by a square law. Based on (2), the curvature is also proportional to the stress in the film, which, in turn, is proportional to the fraction of reacted polymer. Since less polymer mass is required to react, the response time decreases as well. A simple improvement to the current device is to elongate the cantilever by a factor of ten, which should improve the response time by about a factor of two. With these two improvements, the response time should be on the order of seconds.

V. CONCLUSION

We have demonstrated a low-power selective chemical sensing device based on the formation of stress in cross-linked polymer nanofilms covalently attached to thin silicon nitride cantilevers. The value of this paper is the demonstration of enhanced stress formation in highly cross-linked films, which were enabled by iCVD, and the demonstration of a sensing mechanism with simple signal interpretation. Strategies for improving sensitivities have been discussed, and additional cross-linked polymer chemistries can be synthesized by iCVD to sense other analytes.

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REFERENCES


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