

# Polymer Wire Chemical Sensor Using a Microfabricated Tuning Fork

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## ABSTRACT

We have measured the mechanical properties of a polymer wire bridged across the two prongs of a microfabricated tuning fork. The polymer wire is formed by stretching so that it has a built-in mechanical stress. Upon exposure to organic vapors, the stress in the polymer wire diminishes, which is sensitively detected from the changes in the resonance of the tuning fork. We have also shown that by trimming the polymer wire from micrometers down to nanometers the sensitivity and response improve considerably because of an increased surface-to-volume ratio and sharper resonance of the polymer wire-tuning fork system.

Recent advances in nanostructured materials and devices have offered exciting new technologies, including chemical and biological sensors.<sup>1,2</sup> Feldheim et al.<sup>3</sup> explored chemical sensing applications based on the single-electron charging effect in metallic nanoparticles. We showed that the quantized conductance of metallic nanowires is sensitive to molecular adsorption onto the nanowires.<sup>4–6</sup> Penner et al. used arrays of Pd nanowires for a novel H<sub>2</sub> sensor.<sup>7</sup> Several groups reported that the resistance of a single-walled carbon nanotube changes upon exposure to gaseous O<sub>2</sub>,<sup>8</sup> H<sub>2</sub>O,<sup>9</sup> NO<sub>2</sub>,<sup>10</sup> and NH<sub>3</sub>.<sup>10</sup> Lieber's group used boron-doped silicon nanowires to detect biological and chemical species.<sup>11</sup> Huang et al. showed that polyaniline nanofibers provide for more sensitive detection of HCl and NH<sub>3</sub> vapors than the bulk materials.<sup>12</sup> All of these articles report the detection of molecules by measuring an electrical signal of the nanostructured materials or devices. However, because many sensing materials are not conductive, measuring changes in their mechanical properties becomes an interesting choice. One such mechanical approach that has been developed recently is microfabricated cantilevers, which detects bending or changes in the oscillation of the cantilever due to the binding of analyte molecules onto the cantilever.<sup>13–16</sup> Scaling the microcantilevers down to the nanometer scale remains a difficult task. We report here on a method to measure the tensile stress of a polymer wire by attaching it to the two prongs of a microfabricated tuning fork. Using a focused ion beam (FIB), the diameter of the polymer wire was reduced down to the nanometer scale. Exposing the polymer wire to an organic vapor induces a change in the stress, which

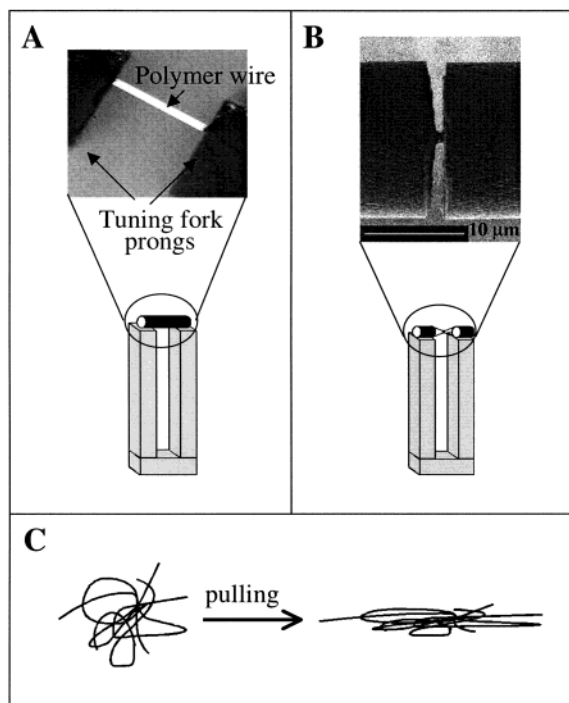
is accurately detected from the change in the resonance frequency of the tuning fork.

Our sensor consists of a quartz tuning fork (Newark Electronics) and a polymer wire attached to the tuning fork (Figure 1). Unlike the commonly used cantilever techniques, the fork converts the force directly to an electrical signal without involving an intermediate signal, such as an optical signal. This eliminates extra sources of noise, simplifies the instrumentation, and, more importantly, allows a compact design for device applications. The widely available commercial quartz tuning fork used in wristwatches is ~2 mm long, ~200 μm wide, and ~100 μm thick. The tuning fork is rather stable because of its relatively rigid structure. A typical fork with a resonance frequency of 32.768 kHz has an effective spring constant of ~20 kN/m. The thermal fluctuation amplitude (rms value) of the prongs is only ~4 × 10<sup>-4</sup> nm at room temperature, based on theoretical calculations and experimental calibrations.<sup>17</sup> The force sensitivity depends on the sharpness of the resonance, which is described by the quality factor, *Q*, defined as the ratio of the resonance frequency to the full width at half-height of the resonance peak. In air, *Q* is ~8000, corresponding to an extremely sharp resonance (Figure 2A). The corresponding force sensitivity is ~5 pN/√Hz (varies as 1/√*Q*).<sup>17</sup> Because of its many unique features, quartz tuning forks have recently been used as force sensors in AFM and near-field optical microscopy.<sup>17–22</sup>

We formed our polymer wire (nitrocellulose/toluene sulfonamide formaldehyde resin) by pulling the polymer gel (dissolved in toluene) under an optical microscope using a translation stage. The individual polymer chains in the wire, which are held in the oriented configuration via noncovalent forces after the evaporation of toluene, align preferentially

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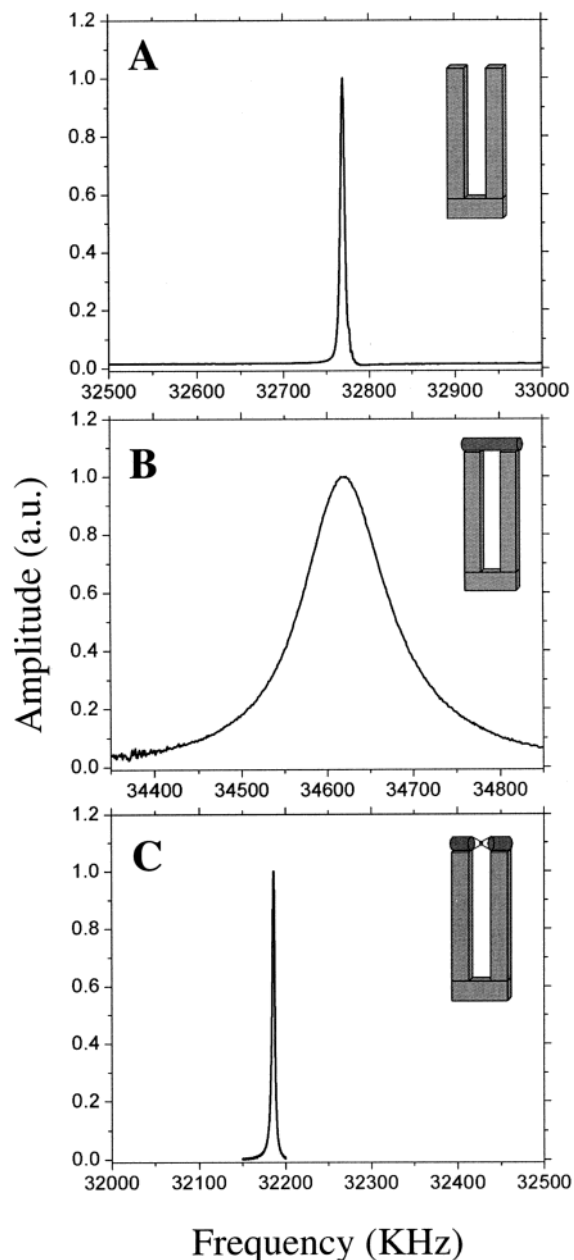
**Figure 1.** Schematic illustrations of a polymer-wire tuning-fork sensor. (A) A polymer wire is bridged across the two prongs of a microfabricated tuning fork. (B) A portion of the polymer wire is trimmed to the nanometer scale using a focused ion beam. The insets in both A and B are scanning electron microscopy images of the wires. (C) The polymer wire is formed by pulling the polymer gel. The individual polymer chains in the wire are forced to align along the pulling direction.

along the pulling direction (Figure 1C). The wire was then glued onto the prongs of the tuning fork. Polymer wires prepared by this method are very uniform, with a typical diameter of a few micrometers (Figure 1A). We reduced the diameter of a small portion of the wire down to  $100 \text{ nm} \times 500 \text{ nm}$  with a focused ion beam system (FIB by FEI Co.) (Figure 1B).

The tuning fork with the attached polymer wire was placed in a small chamber into which a gentle stream of  $\text{N}_2$  was flowing, and the oscillation amplitude as a function of the frequency was determined (Figure 2B). In contrast to the bare fork, the resonance peak is considerably broader ( $Q = 300$ ) because of increased damping of the polymer wire. The resonance frequency of the fork with the polymer wire is  $\sim 2 \text{ kHz}$  higher. This increase in the resonance frequency is related to Young's modulus of the polymer wire, which is given by

$$E = \frac{2Lk_{\text{fork}}}{Af_0} \Delta f_0 \quad (1)$$

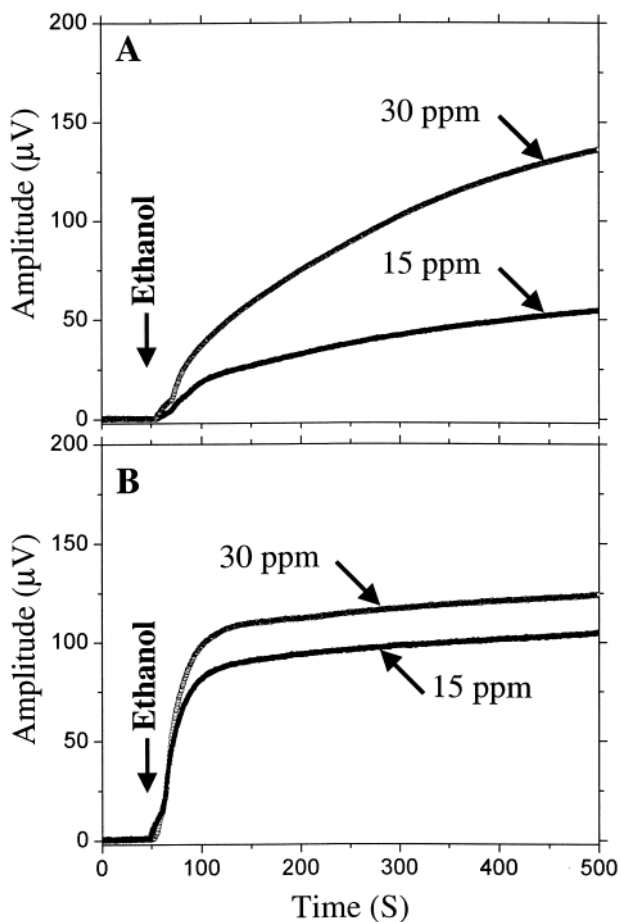
where  $L$  and  $A$  are the length and cross-sectional area of the polymer wire, respectively,  $k_{\text{fork}}$  and  $f_0$  are the effective spring constant and resonance frequency of the bare fork, respectively, and  $\Delta f_0$  is the shift in the resonance frequency in the presence of the polymer wire. The change in the effective mass due to the polymer wire is small, as discussed later,



**Figure 2.** Oscillation amplitude vs frequency plots show well-defined resonance peaks of (A) a bare fork, (B) a fork with a micrometer-sized polymer wire, and (C) a fork with a polymer wire cut with an FIB.

and thus neglected in the above equation. Because  $L = 200 \mu\text{m}$ ,  $A = 1.8 \times 10^{-4} \text{ mm}^2$ ,  $k_{\text{fork}} \approx 20 \text{ kN/m}$ ,  $f_0 = 32.768 \text{ kHz}$ , and  $\Delta f_0 = 2 \text{ kHz}$ , we have  $E = 3 \times 10^9 \text{ N/m}^2$  according to the above relation. This demonstrates a simple method of determining the properties of a polymer wire.

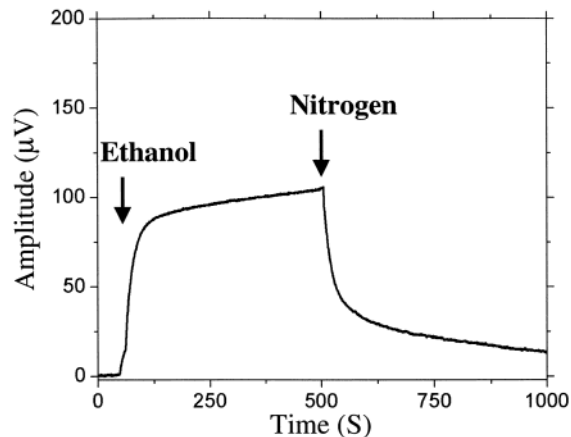
To test our sensor, the stream of  $\text{N}_2$  was redirected to pass through a flask containing ethanol to carry the vapors into the chamber. We controlled the vapor pressure by controlling the temperature of the liquid ethanol in the flask. To monitor the entire process, we induced near-resonance oscillations in the tuning fork and detected the change in the oscillation amplitude with a lock-in amplifier. Exposing the polymer wire to ethanol vapor changes the resonance frequency and thus the oscillation amplitude. Figure 3A shows the responses



**Figure 3.** (A) Response of a tuning fork with a micrometer-sized polymer wire upon exposure to 15 and 30 ppm ethanol. (B) Response of a tuning fork with an FIB cut polymer wire upon exposure to 15 and 30 ppm ethanol.

of a thick ( $\sim 15 \mu\text{m}$ ) polymer wire upon exposure to 15 and 30 ppm of ethanol. The oscillation amplitude changes quickly in the beginning and then slows down. As expected, the change for 30 ppm is quicker and larger than that for 15 ppm. We note that the small kink in the initial portion of the curve (shown in Figure 3) is due to the disturbance associated with the injection of ethanol into the chamber. Exposure of the same fork to 180 ppm (ethanol vapor at room temperature) resulted in the complete saturation of the sensor due to large shifts in the resonance frequency. We have performed the same experiment using a bare tuning fork and have detected no visible changes in the oscillation amplitude. We have also exposed the fork with the polymer wire to acetone vapors and have observed similar changes but with a greater magnitude because of the higher solubility of the polymer in acetone than in ethanol.

In principle, the adsorption of organic vapors can change both the mass and the spring constant of the polymer wire. The former one should result in a decrease of the resonance frequency, which is the basis of the quartz microbalance technique (QCM). In our case, the mass of the polymer wire is  $\sim 10^{-5}$  mg, and the mass increase due to adsorbed organic vapors is much smaller than the effective mass of the tuning fork ( $\sim 1$  mg), so the mass effect is negligible. We believe



**Figure 4.** Oscillation amplitude of a tuning fork with an FIB cut polymer wire changes reversibly upon the adsorption and desorption of ethanol vapors.

that the change in the spring constant of the polymer wire is the dominant effect. This conclusion is confirmed by the observation that a broken polymer wire produces no changes in the resonance frequency upon exposure to organic vapors.

The sensitive dependence of the effective spring constant of the polymer wire on the organic vapors can be understood on the basis of the following considerations. When the polymer is pulled into a wire, the individual polymer chains are forced to align along the pulling direction (Figure 1C). After the organic solvent is evaporated, the polymer chains are trapped in this configuration via noncovalent interactions with the neighboring polymer chains. By exposing the wire to an organic vapor, the organic molecules penetrate into the wire and “redissolve” the polymer chains, thus softening the polymer wire.

To improve the sensitivity and response of the polymer-based sensor further, we reduced the diameter of a small portion of the polymer wire with FIB. The cross section of the FIB cut portion is rectangular with dimensions of  $100 \text{ nm} \times 500 \text{ nm}$ . We performed the measurement in a similar fashion to that of the micrometer-sized polymer wire. Figure 3B shows the response of the oscillation amplitude upon exposure to 15 and 30 ppm of ethanol. The amplitude of the FIB cut polymer wire changes much more sharply upon exposure to organic vapors. The amplitude recovers after removing the vapor source and flushing the chamber with  $\text{N}_2$  (Figure 4). The recovery is at a much slower rate as ethanol trapped in the wire diffuses out slowly.

This experiment demonstrates the improved sensitivity and response by decreasing the size of the polymer wire, which can be understood by the following considerations. The spring constant of the entire polymer wire is dominated by the narrowest portion of the polymer wire. Because the thin portion has a greater surface-to-volume ratio, organic vapors can quickly diffuse into the polymer and change the effective spring constant. Another reason for the improved sensitivity is the reduced damping after trimming the wire with FIB. As shown in Figure 2, the  $Q$  value of the FIB trimmed polymer wire is about  $\sim 4000$ , which is close to that of the bare tuning fork. It can be shown that when inducing near-

resonance oscillations in the fork, the amplitude change due to the shift in the resonance shift is approximately proportional to  $Q$ .

In summary, we have demonstrated a simple way to measure the mechanical properties of a thin polymer wire using a microfabricated quartz tuning fork. Upon exposure of the wire to organic vapors, the tendency of the organic solvent to dissolve the polymer wire results in a large change in the mechanical properties of the polymer, which can be used for sensor applications. We have also shown that the sensitivity and response can be significantly improved by reducing the diameter of the polymer wire to the nanometer scale.

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