Spiral springs and microspiral springs for chemical and biological sensing

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This work demonstrates that a mechanical device based on spiral spring or microspiral spring has a broad range of applications for detection of chemical and biological species. The surface stress changes or polymer volume changes on one side of the spiral spring extend or contract a spiral spring. The macrosize spiral spring can be used for power-free sensor development. © 2006 American Institute of Physics. [DOI: 10.1063/1.2172407]

The first crude hygrometer was built in the 1400s by da Vinci. Folli invented a more practical hygrometer in 1664. In early 1700, Hooke invented the first balance spring or spiral spring that improved the meteorological instruments such as the barometer, anemometer, and hygrometer, etc. 1 In a dial hygrometer, a humidity sensitive polymer coated strip spiral spring is attached to a dial to indicate humidity. The spiral springs undergo extension or contraction due to moisture absorption by the absorption to one side of the spiral spring. When the relative humidity increases, the polymer swells which extends the spiral spring and pulls the dial hand. At a low relative humidity, the polymer releases the tension on the spiral spring, which allows the dial hand to move in the opposite direction.

Although the bilayer-based dial barometer, thermometer, and hygrometer have been used for several centuries, no other sensors have been developed based on this concept. Recently, we realized that this bilayer-based dial hygrometer might be used as a universal tool for the detection of chemical and biological species by depositing a chemical specific coating on one side of the spiral spring. If appropriately designed, the concentration of chemicals can be directly read by human eyes by dial hand movement or be accurately measured in the electrical domain by observing the change in conductance or resistance of a piezoelectric or piezoelectric material coated onto the spiral spring. In this letter, we report on the proof-of-concept sensor applications using a platform based on spiral springs and microspiral springs.

The spiral spring component can be made of any thin, elastic materials, including polymers, composites, metals, alloys, etc. The size of the spiral spring depends on the intended application. We used a brass spiral spring for power-free chemical measurement. The dimensions of this spiral spring were 75 μm in thickness, 3 mm in width, 10 cm in length in the extended form.

In a simple demonstration of chemical species detection in air, we developed an alcohol sensor by coating one side of the spiral spring with a thin layer of polypyridine (PV), an alcohol sensitive polymer. 2 The dial hand of the PV coated spiral spring moved to the right upon exposure to alcohol vapor as shown in Fig. 1, indicating the swelling of the PV polymer. We named the device a dial alcoholmeter—an inexpensive device for alcohol measurement.

Stimuli-responsive hydrogels 3–7 were used to confirm the sensing ability of the spiral spring in solutions. Since intelligent hydrogels swell in response to the concentration of particular analytes and the gel volume is a function of analyte concentration, the swelling of the gel changes will extend or open the spiral spring and drag the movement of the dial hand.

In one proof-of-concept test, a hydrogel that contains amino groups was used for pH measurement. An acrylamide precursor 8 solution was spread on a brass strip, and the strip was exposed this strip to an UV light to form a hydrogel on the strip. The strip was then wound up to a spiral spring. A dial hand was attached on the center of the spiral spring. The resulting gel coated spiral spring was equilibrated in a pH = 7.0 buffer solution for 1 day before testing in different buffer solutions at different pH values. All the phosphate buffer solutions had the same buffer concentration (0.01 M) and ionic strength with different p H. When the pH was > 7, the spiral spring dial hand turned left indicating that the gel had contracted. The minimum gel volume occurs at high pH where the NH2 groups are saturated. When the pH was < 7, spiral spring turned right indicating that the gel had swelled (figure not shown). At lower pH, the amino groups of the gel tend to be protonated, and the gel expands because of increased electrostatic repulsion between the cationic chains and the increase in the Donnan osmotic pressure. 7

In another experiment, a glucose oxidase (GOx) containing hydrogel modified spiral spring was tested for the measurement of glucose. GOx is a highly specific enzyme that oxidizes 9,10 glucose and produce gluconic acid and hydrogen peroxide

\[ \beta \rightarrow D - \text{glucose} + O_2 + H_2O \]

Glucose Oxidase

\[ \text{D} \rightarrow \text{gluconic acid} + H_2O_2. \]

The generation of gluconic acid is capable of promoting electroosmotic swelling of the gel due to the formation of charged ions, including gluconate and proton, and also the subsequent swelling of the gel. As expected, when the spiral spring was placed in a glucose concentration, the spiral spring dial hand turned left indicating that the gel had contracted (figure not shown).
We expect to develop an array of spiral spring based sensors, where each individual sensor will detect different chemicals or biomolecules and different concentration ranges. The dial hand movement will be read from the calibrated numeral dial face for different analytes in solutions. This technology may provide a simple, power-free kit for environmental or clinical diagnostics. Since most intelligent gels are relatively homogeneous materials that shrink or swell uniformly with no dramatic change in shape, the spiral spring expansion is reversible and reproducible.

The spiral spring movement can be readily observed by human eyes and it advances as a cost-effective and power-free device. However, due to the relative large size, the dynamic response time of this spiral spring device can not compete with many other micro- and nanosensors. It is expected that a spiral spring device at micro- or nanoscale size will provide an outstanding sensor platform with an improved dynamic response, greatly reduced size, and integration of micromechanical components with on-chip electronic circuitry. In this work, we fabricated a SiO$_2$/Si/SU-8 (Ref. 11) trilayered microspiral spring for sensing validation. The piezoresistive property of the doped Si was used to determine the adsorption/absorption induced microspiral spring extension.

The simulation and detailed fabrication process will be reported somewhere else. Briefly, the fabrication process for a piezoresistive SiO$_2$/Si/SU-8 microspiral spring has four steps: first, the fabrication of the piezoresistive Si spiral spring by a typical photolithography method using dry plasma etching; second, the deposition of the electrodes that connect the two ends of the spiral spring by the metallization and “lift-off” method; third, oxidation of the surface of silicon; fourth, patterning of a SU-8 layer on one side of the microspiral spring. A scanning electron microscopy (SEM) picture of a fabricated microspiral spring is shown in Fig. 2.

To demonstrate the concept of microspiral spring based sensors, we modified the SiO$_2$ side of a microspiral spring with a thin film of amines by treating the spiral spring with aminopropyltriethoxysilane according to a typical silica surface modification procedure. As expected, the resistance of the microspiral spring changed in an acidic environment as shown in Fig. 3(a). Our results showed that the resistance of the microspiral spring changed from $5.50 \pm 0.01 \text{ M}\Omega$ to $5.78 \pm 0.01 \text{ M}\Omega$ upon exposure to a 2.1% acetic acid vapor in air. It is known that when piezoresistive material such as doped silicon is under stress, its resistance changes. The results suggested that the interaction of acids with amino groups on the silicon surface produced changes in free surface energy that extended the spiral spring and resulted in the subsequent resistance change of the spiral spring. One control experiment showed that a microspiral spring without amine film did not change its resistance upon exposure to acids, ruling out the possible interaction of acetic acid molecules with silicon surface or SU-8 polymer. Another control experiment was performed on an aminopropyltriethoxysilane modified SiO$_2$/Si strip. The dimension of this strip was the same as an extended microspiral spring, i.e., 7.7 mm in length, 50 $\mu$m in width. The results showed that the resistance change of the strip was negligible upon exposure to a 2.1% acetic acid. These experiments confirmed the surface stress induced microspiral spring extension.

The microspiral spring functions in a fashion similar to a microcantilever, which has been widely investigated recently. An amino treated silicon microcantilever was used for comparison as shown in Fig. 3(b). It’s apparent that the base line of the microspiral spring device was more stable than that of microcantilevers. The microspiral spring device underwent less drifting than the microcantilever. Furthermore, the $\Delta R/R$ change of the microspiral spring upon exposure to a 2.1% acetic acid vapor is significantly more sensitive than the 0.04% change of the amino treated silicon cantilever sensor under the same conditions. One disadvantage of the microspiral spring device was its longer response time than that of the microcantilever. For instance, the resistance change of the microspiral spring reached its maximum
in 20 s after exposure to acetic acid, while it took only approximately 5 s to reach a plateau for a microcantilever.

In conclusion, we have presented a platform based on spiral springs and microspiral springs can be used for detection of chemical and biological species both in air and solutions. Beside the polymer and silane film studied in this work, many other approaches can also be used to immobilize the molecular recognition agent onto the spiral spring surface, such as self-assembled monolayers on gold, surface conjugation chemistry, self-assembled monolayer, etc. Using the same spiral spring/microspiral spring and even nanospiral spring device, numerous molecular, or biomolecular recognition agents could be immobilized onto the spiral spring surface for various chemical/biomolecule detection. The chemical selectivity can be achieved by a wide variety of antibody-antigen interactions, protein-protein interactions, DNA hybridizations, and chemical recognition by a number of selective host molecules such as crown ethers, calixarenes, cyclodextrins, cryptand derivatives, etc.

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9 The precursor solution contained 2.1 mmol of acrylamide, 0.27 mmol of 2-dimethylamino ethyl methacrylate, 0.072 mmol of N,N'-methylenebisacrylamide and 0.08 mmol of an UV photoinitiator such as diethyoxyacetophenone dissolved in 3 ml of water.
10 SU-8 is a thick, near-UV negative photoresist used for microelectromechanical systems fabrication.