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Microsensors to Monitor Missile Storage and Maintenance Needs

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MICROSENSORS TO MONITOR MISSILE STORAGE AND MAINTENANCE NEEDS

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Abstract

Accurate assessments of reliability and condition based maintenance can only be implemented where a good understanding of ammunition stockpile condition exists. Use of miniaturized intelligent sensors provides an inexpensive means of nondestructively gaining insight into stockpile condition while keeping costs low. In the past, evaluation of ammunition lifetimes has utilized humidity, temperature, pressure, shock, and corrosion. New technologies provide the possibility of obtaining these environmental parameters, as well as a number of other indicators of propellent degradation, including NO_x by utilizing a microsensor with capability for remote wireless monitoring.

Micro-electro-mechanical systems (MEMS) like microcantilevers promise to revolutionize the field of sensor design. In the automobile industry, micromachined acceleration sensors are now used for triggering airbags and pressure sensors adjust the air-fuel intake ratio in the engine. By applying coatings to the sensor's surface the behavior of the microdevice can be measurably altered to respond to chemical species as demonstrated by ORNL using microcantilevers to detect mercury vapor and humidity.

To fully realize the potential revolution in chemical sensors offered by MEMS technology, there is a need to develop materials for use as sensitizing coatings for specific detections. For example, zeolites are thermally stable aluminosilicate framework structures used commercially as molecular sieves, catalysts, ion exchangers and chemical absorbers. They show excellent selectivity and have the additional benefit of selective thermal desorption properties. Ultimately, single-chip detectors with electronics and telemetry could be developed with conceivably hundreds of individual microsensors on each chip to simultaneously monitor, identify, and quantify many important chemical species for ammunition as well as measure environmental parameters.

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Introduction

The Army has been interested in accessing the condition of ammunition in storage locations for some time. During Operation Desert Storm, this need became more acute with extreme conditions faced there. At that time, a palm of the hand sized data collection system was commercially available which measured temperature, humidity and pressure. This data logging system provided a 10 year battery life in a portable package which was capable of storing information until it could be downloaded to a host computer. However, there were drawbacks to this instrumentation like cost, robustness, and the need for additional measurements not provided by the logger.[1]

Follow-on work aimed at characterization of storage environments was funded by the Army which provided measurements of corrosion and shock. The first of these was a larger system deployed in an igloo. This system had more precise temperature measurements, humidity sensors which could tolerate condensing environments, and measurement of corrosion. One important limitation of this system was that the corrosion sensors had limited life in moderate to severe environments. Additionally, the system was not intended for applications where portability is important. More recent initiatives included development of a small system for measuring and storing temperature, humidity, pressure, corrosion and shock.

The wisdom of funding the development of systems to collect environmental data is supported by problems encountered in M829 tank rounds and missiles which were used in Operation Desert Storm. Better knowledge of environmental conditions faced by our weapon systems will result in more accurate assessments of stockpile viability as well as provide assistance in maintaining ammunition.

Measuring environmental parameters seen by weapon systems requires miniature cost-effective sensors capable of measuring a variety of parameters. One technology currently being researched at Oak Ridge National Laboratory (ORNL) which has promise in this area is a small microcantilever. An array of these devices serves as a universal sensor platform. In addition to measurement of temperature, humidity, pressure, shock and corrosion, there is potential for measuring chemical species like NO_x from propellent degradation or hydrazine. Additionally, these measurements can all be made on a single small sized substrate which would contain conditioning electronics as well as telemetry. The balance of the paper will discuss this exciting new technology.

Microcantilever Sensor Chips

Environmental monitoring, industrial-process control, and biomedical monitoring all rely upon analyses performed by a variety of means. Obviously when possible, real-time detection using high-performance sensors is greatly preferred over cumbersome and time-consuming sampling and laboratory analysis. Unfortunately, most sensors developed to date have been limited in detection ability and the number of components that can be sensed. Also, each requires electronic conditioning, packaging, and physical wiring, which impedes widespread, practical implementation.

These limits may be alleviated soon with the advent of new micro-electro-mechanical systems (MEMS). For the past two decades, active-control electronic technology has coupled computer circuitry within everyday products. Enabling key factors include: very low cost and modular design. Electro-mechanical devices (i.e., those that add mechanically responding components to electronic-circuit chips) can also be mass manufactured by a similarly rich set of tools and the microlithographic technologies developed for computer circuitry. Again, the key operative factors are low cost and modularity.

One of the simplest mechanical structures to machine is a springboard (or "cantilever"), which can be readily fabricated on silicon wafers and other materials. Several can fit across the period at the end of this sentence. Such a small cantilever, hanging off the edge of a support piece, deflects quite easily even under minuscule forces. In fact, micromachined cantilevers were developed for a new microscope sensitive enough to feel individual atoms. The atomic force microscope (AFM), first demonstrated by IBM researchers in 1986, uses a cantilever to contact a sample surface with a light enough force so as not to disturb the atomic arrangement. As this tiny stylus scans the surface, the deflection is monitored with sub-atomic precision. For the last several years, our group has been developing applications using the AFM. While using the instrument, it occurred to us that with this sensitivity it is possible to discern changes in the cantilever induced by environmental effects (Fig. 1).

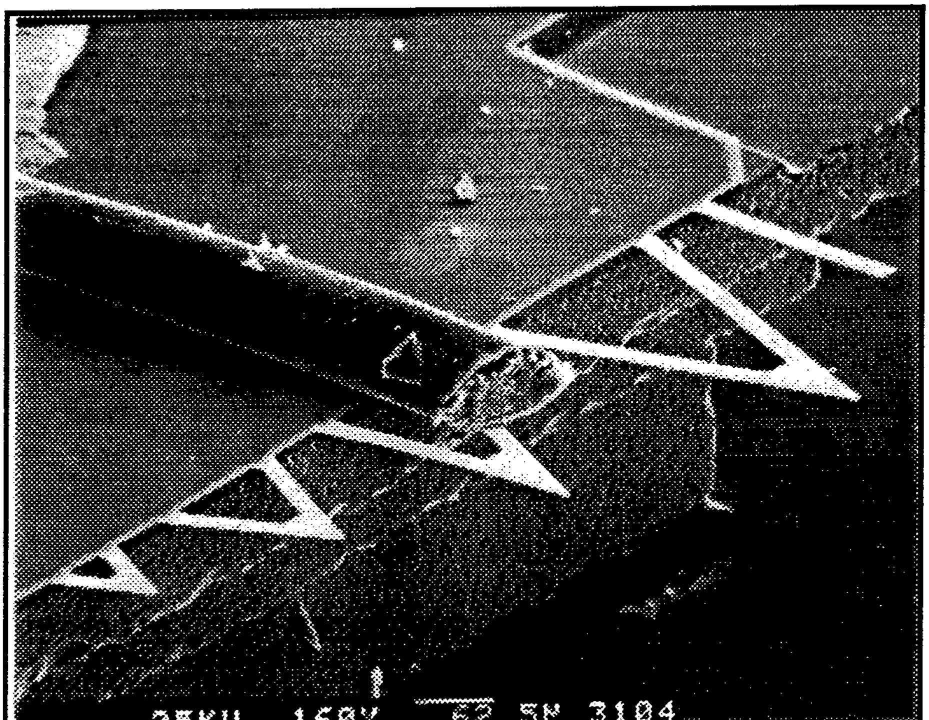

Figure 1. Microcantilevers can be used as a sensitive microsensors as coatings are individually applied (length: 50-200um, width: 10-30um, thickness 0.1-10um, shown with human hair for perspective).

Coatings applied to the cantilever selectively absorb chemical species and change the natural resonant frequency of the cantilever because of the added mass. Gold-coated cantilevers were first tested to selectively absorb mercury vapor. What was observed appeared to contradict the idea that added mass would lower the resonant frequency. The frequency of a simple mechanical oscillator is:

$$f = \frac{1}{2\pi}\sqrt{\frac{K}{m}}$$

where is the spring constant and is the effective mass. For an increase in mass, the resonant frequency, should decrease. However, the frequency went up when the cantilever was exposed to the mercury, indicating that the spring constant was being more strongly affected than the mass. The shift in resonant frequency can be written as:

$$\Delta f = \frac{f}{2}\left(\frac{\Delta K}{K} - \frac{\Delta m}{m}\right)$$

Mass and spring-constant effects can be separated by selecting where the absorption occurs. By applying the coating at the end of the cantilever, the frequency was seen to decrease as expected (Fig. 2). For coatings applied near the base where flexing is the greatest, changes in spring constant control the frequency. In fact, such coatings can also produce a static stress on the cantilever, and the deflection, measured with the same sensitivity utilized in atomic force microscopy, can be related to material absorbed.[2]

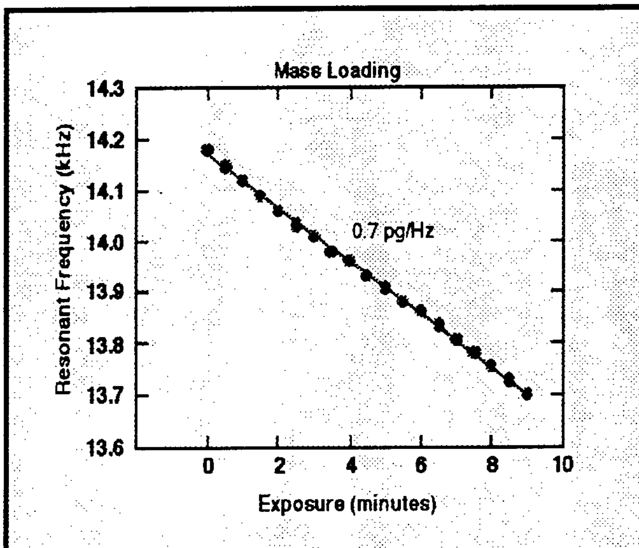

Figure 2. Response of gold-flashed cantilever to mercury vapor.

Consequently, microcantilevers are a universal platform to base electro-mechanical sensors for measuring a multitude of physical, chemical, and even biochemical factors, depending upon the selection of the coating.[3] By applying a thin layer of gelatin or other hydroscopic material, humidity can be sensed. We found that silicon-nitride cantilevers coated with gold on one side are quite sensitive to pH changes.

A number of chemically derivatized coatings are already being used in other electro-mechanical sensors, such as surface-acoustic-wave (SAW) devices. These coatings can be readily employed on their much smaller microcantilever cousins. To date we have used coated microcantilevers to detect mercury vapor, humidity (Fig. 3)[4], natural gas, gas mixtures, toluene, and, by selective electrode position, lead in water. Detection limits have yet to be fully explored, but parts-per-billion to parts-per-trillion appear to be well within reach in some cases.

One of the more promising techniques for selective chemical species detection is the use of zeolites. Zeolites are thermally stable aluminosilicate framework structures used commercially as molecular sieves, catalysts, ion exchangers and chemical absorbers. There are over 100 known structure types each with

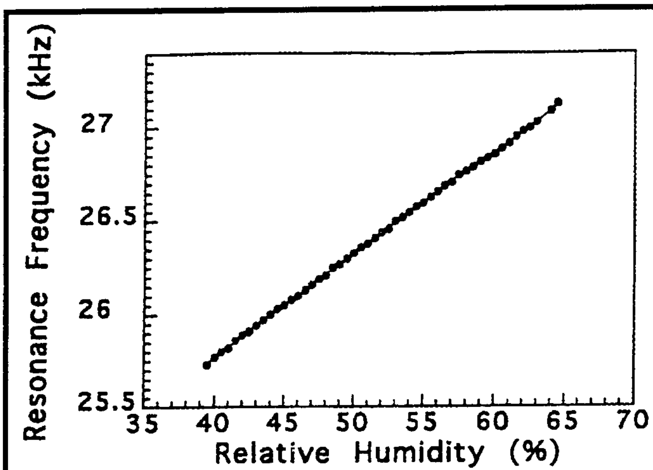

Figure 3. Resonant-frequency response of a gelatin coated cantilever to humidity (23 nm coating thickness).

specific pores and cages. Within each structure type there can be numerous analogs providing additional potential for chemical selectivity. In addition to selective absorption, zeolites have temperature selective desorption properties. The combination of these characteristics expands the potential applications of zeolitic coatings to act as chemical sensors. Because of their stable structures, numerous methods can be investigated for applying zeolites to the MEMS surface. Ultimately, the development of chemical detectors using an array of 100 to 1000 individual sensors would have the capacity to simultaneously monitor, identify, and quantify a wide number of important chemical species.[5]

We are also working on a miniaturized biosensor employing microcantilevers operating in one of two modes. The first uses biosensitive coatings that selectively absorb species and affect cantilever bending or resonance. An example is the detection of a biotoxin using its monclonal antibody as a cantilever coating. Working with Steve Kennel, Bruce Jacobson, and a graduate student, Aravind Subrumanian, we have seen very encouraging results with a sensitivity at the parts-per-trillion level. The second biosensor scheme exploits an intrinsic property of chemical reactions - calorimetry. Specific labeling or electron transfer is eliminated as only temperature changes need to be measured. Since most chemical reactions are associated with a change in heat, calorimetry is a general detection scheme with the potential to selectively identify a wide range of compounds. Our initial test uses the immobilization of an enzyme, glucose oxidaze, which specifically reacts with glucose in solution, producing a recognizable calorimetric signal. The tiny thermal mass and sensitivity of the cantilever makes calorimetry possible on this scale.

Physical environmental conditions can be measured by recording their effects upon cantilever operation. Temperature changes of the order of microdegrees can be sensed with a thermally expansive coating (bimetallic effect) with sub-millisecond response. With such temperature sensitivity, infrared images can be recorded.[6] We also demonstrated that the viscosity of liquids and gases can be measured over a range of 10,000 using a single cantilever.[7] Similarly, the effects of small atmospheric-pressure changes can be felt in the resonance of a vibrating cantilever. As a vane in a flowing stream, a cantilever could be used to monitor velocity for flow control. Cantilevers can be tuned to selectively pick up acoustic vibrations. Effects of exposure to ultraviolet radiation can be sensed by choosing the proper polymeric coating, and local radiation dosimetry is even possible by recording radiation-induced changes in cantilever properties.

The trend in miniaturization of intelligent sensors couples very well with versatility of cantilever arrays. The cantilever signal can be readout optically but designs using piezoresistive and capacitive pickups are well suited to integration with on-chip electronic circuitry. The electronic processing could further incorporate analog intelligence to decouple non-selective responses to environmental effects. Thus, the need to find coatings that individually respond only to a particular chemical is obviated. Micromachining technologies currently available could be used to make multitarget sensor arrays involving hundreds of cantilevers, analog processing, and even local telemetry on a single chip (Fig. 4). The number of sensing elements in a sensor array can be used for lower noise, much higher selectivity, and increased robustness. Simplicity, low power consumption, potentially very low cost to manufacture, inherent compatibility with array designs, and the ability to operate in air or liquid make cantilever sensors very attractive for a variety of applications.

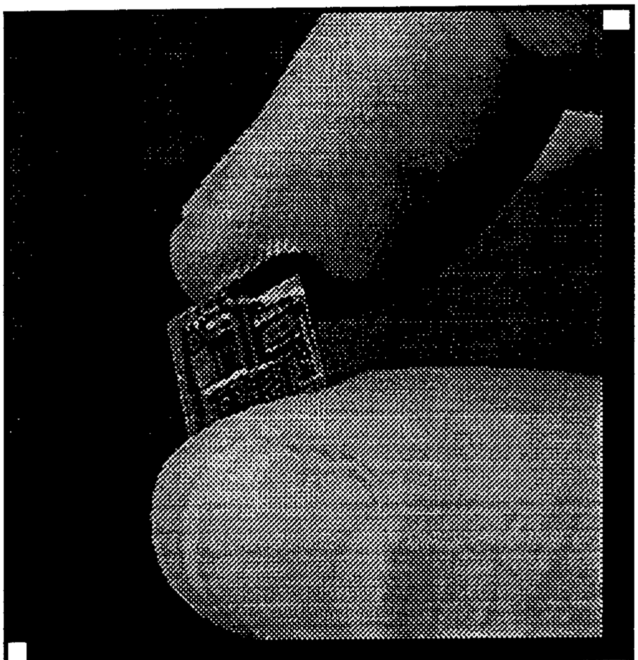

Figure 4. Currently available array containing hundreds of cantilevers.

There are a number of challenges to overcome before MEMS sensors come into widespread use. The technology for designing and simulating electronic chips is well advanced. Software to integrate electronic, mechanical, and fluidic designs is still in its infancy, yet huge investments presently being made will soon accelerate the design of fully integrated devices. The effects of environmental influences on coatings and cantilevers will need to be fully characterized and incorporated into data libraries, so that a prospective chip can be completely characterized before hardware fabrication. Additional coatings and attachment methods will need to be developed and added to the libraries. The development of on-chip microfluidics will also be needed to facilitate some applications. Material stability is an issue that potentially limits long-term reliability in harsh conditions and will need to be addressed. Just as similar challenges have been met by the semiconductor industry, we believe these will be overcome.

Applications are widespread from military instrumentation to functions in consumer appliances, factories, and hospitals. This technology is particularly beneficial where multiple factors must be analyzed and screened on-chip. Not only will existing monitoring instrumentation be improved but microcantilevers will give rise to new applications involving embedded sensing, infrared surveillance, medical diagnostics, pollution detection,, clinical analysis, and food processing, as just a few examples. Telemetry will enable the deployment of fieldable devices to relay pertinent data to central collection stations, the use of mobile units worn or carried by personnel, and the replacement of wired sensors in some applications. Currently ORNL is designing and demonstrating a microfabricated chip with built-in electronic processing and telemetry. Additionally, coatings and methods for applying them are being developed to detect different species. This is essential for the technology of tomorrow.[8]

References

1 D. K. Mee, D. W. Carver, L. E. Seiber (1991). "Evaluation of Miniature Dataloggers for Use in Harsh Environments," *Proceedings of the Predictive Technology Symposium.*

2 T. Thundat, E. A. Wachter, S. L. Sharp, and R. J. Warmack, (1995). "Detection Mercury Vapor Using Resonating Cantilevers," *Appl. Physics. Lett.* **66**, pp. 1695-7.

3 E. A. Wachter and T. Thundat, (1995). "Micromechanical Sensors for Chemical and Physical Measurements," *Rev. Sci. Instrum.* **66** (6), pp 3662-7.

4 T. Thundat, G. Y. Chen, R. J. Warmack, D. P. Allison, and E. A. Wachter, (1995). "Vapor Detection Using Resonating Microcantilevers," *Analytical Chemistry* **67**(3), pp. 519-21.

5 C. Hubbard, R. Peascoe and W. Porter, P. I. Oden, and R. J. Warmack (1997, unpublished). *Demonstration of the Deposition of Zeolites on Micro-Electro-Mechanical-Systems for Use as Selective Chemical Sensors.*

6 P. I. Oden, P. G. Datskos, T. Thundat, and R. J. Warmack, (1996). "Uncooled Thermal Imaging Using a Piezoresistive Microcantilever," *Appl. Phys. Lett.* **69** (21), pp. 3277-9.

7 P. I. Oden, G. Y. Chen, R. A. Steele, R. J. Warmack and T. Thundat, (1996). Viscous Drag Measurements Utilizing Microfabricated Cantilevers," *Appl. Phys. Lett.* **68** (26), pp. 3814-6.

8 T. Thundat, P. I. Oden, and R. J. Warmack. "NanoSensor Array Chips," Appliance Manufacturer, April 1997, pp. 57-58.

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