Ultra-responsive thermal sensors for the detection of explosives using Calorimetric Spectroscopy (CalSpec)

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ABSTRACT

We have developed a novel chemical detection technique based on infrared micro-calorimetric spectroscopy that can be used to identify the presence of trace amounts of very low vapor pressure target compounds. Unlike numerous recently developed low-cost sensor approaches, the selectivity is derived from the unique differential temperature spectrum and does not require the questionable reliability of highly selective coatings to achieve the required specificity. This is accomplished by obtaining the infrared micro-calorimetric absorption spectrum of a small number of molecules absorbed on the surface of a thermal detector after illumination through a scanning monochromator. We have obtained infrared micro-calorimetric spectra for explosives such as TNT over the wavelength region 2.5 to 14.5 μm. Thus both sophisticated and relatively crude explosive compounds and components are detectable with these ultra-sensitive thermal-mechanical micro-structures. In addition to the above mentioned spectroscopy technique and associated data, the development of these advanced thermal detectors is also presented in detail.

Keywords: calorimetric spectroscopy, thermo-mechanical, bi-material, penta-lever

1. INTRODUCTION

There has recently been a need, and associated difficulty, in measuring the presence of trace amounts of explosive agents (mines) with great sensitivity and selectivity. Indirect methods such as thermal infrared imaging, ground penetrating radar and magnetic signatures are often very useful, but suffer from high false detection rates depending on the test site conditions. The more direct route of detecting and identifying the molecules of explosive materials themselves, has two possible approaches. The first approach is to transform a respectable laboratory instrument into a field-ready system. This typically results in a relatively large, expensive, fragile and difficult to implement system. However the data is typically beyond reproach. The other approach is to rely on recently developed sensor technologies that may possess the required sensitivity, but often lack the chemical selectivity to perform the required detection. These are typically gravimetric devices that rely on elusive chemically selective coatings deposited onto sensors such as surface acoustic wave, quartz crystal oscillators, micro-cantilevers, etc. Thus what is required for this type of detection problem is a reliable, rugged, sensitive, selective, micro-instrument in a sensor sized package. The calorimetric spectroscopy (CalSpec) technique lends itself very well to the above mentioned parameters. Although no single...
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technology has thus far shown itself to be the entire solution in all situations, a CalSpec based approach can definitely play a significant role in dealing with the explosive/mine detection problem.

2. CALORIMETRIC SPECTROSCOPY

Detecting the presence and determining the identity of molecules using micro-calorimetric spectroscopy can be broken down into two main steps. In the first step the vapor phase sample is allowed to interact with the surfaces of extremely sensitive thermal-mechanical micro-structures that may be coated with an appropriate chemical layer selective to the family of the target chemicals. Since in our method only moderately selective chemical coatings are needed, the chemical selectivity is determined by a spectral "signature". This is in stark contrast with multiple sensor technologies presently being promoted for trace chemical detection. Depending on the choice of thermal-mechanical micro-structures, the initial molecular adsorption can induce surface stress changes that provide a trigger, indicating a need to provide analysis on the adsorbed molecules. In the second step, a photo-thermal spectrum is obtained for the molecules adsorbed on the detector surface by scanning a broadband wavelength region with the aid of an infrared source and a monochromator. Because different micro-mechanical elements will be exposed to different wavelengths, a sensitive photo-thermal signature response can be obtained. The temperature changes of those particular detector elements is proportional to the number of photons absorbed which, in turn, is proportional to the number of molecules adsorbed on the detector surface. Photo-thermal spectra are very similar to conventional infrared spectra and can be used to uniquely identify the adsorbed molecules. Figure 2 shows a TNT CalSpec spectrum. It exhibits strong thermo-mechanical deflection responses corresponding to the traditional absorption peaks located at the micro-structure element positions that are at the correct absorption wavelength. The approximately mono-layer chemistry adsorbed on the micro-structure elements was scanned to produce the TNT temperature differential spectrum.

**Figure 1.** Schematic representation of the principle of micro-calorimetric spectroscopy. Photons of different wavelength irradiate different thermal detectors configured as a linear array. Molecules adsorbed on the surface of thermal-mechanical elements absorb photons and a differential photo-thermal spectrum is obtained.

**Figure 2.** Photothermal response of a micro-structure thermal-mechanical element exposed to TNT as a function of wavelength (solid curve).

**Figure 3.** Experimental set-up for thermo-mechanical response measurement (CalSpec data) for both displacement distance \( Z \) and rotation angle \( \Theta \).
3. THERMO-MECHANICAL RESPONSE DETERMINATION

The thermo-mechanical response of the micro-structure used in this work can be readily determined by multiple methods, including optical beam, optical diffraction, capacitance, electron tunneling, piezoresistance, and other conceivable methods. In this work we concentrated on the optical beam redirection method which is the primary method used in ultra-sensitive atomic force microscopy (AFM). A simple laser beam redirection arrangement was used to monitor the micro-structure thermal response. As can be seen from figure 3, a diode laser focused onto the tip of the micro-structure will reflect toward a multi-element silicon photodiode detector. Heating of the micro-structure by the position sensing probe laser is minimized by the gold coated surface that forms the bi-material structure. Redistribution of energy across the multiple photodiode elements can readily be detected as a result of heating and related to less than a nanometer movement of the micro-structure tip. For the initially demonstrated thermo-mechanical devices we adapted relatively simple displacement measurement and modeling techniques. However, the more recently configured ultra-sensitive devices produce a rotation with often minimal displacement. This rotation is now a significant factor in measuring the thermo-mechanical response of these devices and must be taken into account. Thus for a temperature variation from \( T_0 \) (initial straight position), to a new temperature \( T \), the angular deflection \( \Theta \) (radians) is given by equation 1 and the linear displacement \( Z \) is given in equation 2. In these equations, \( l \) and \( t \) are the bi-material length and thickness, respectively. The coefficients of thermal expansion and the Young's moduli are represented by \( \alpha \) and \( E \), respectively. The variable subscripts refer to the parameters associated with the two materials of the bi-material system.

\[
\Theta_{\text{max}} = \frac{6 \left( t_1 + t_2 \right) l}{t_2^2} \frac{(\alpha_2 - \alpha_1)}{4 + 6 \frac{t_1}{t_2} + 4 \frac{t_1^2}{t_2^2} + \frac{E_1 t_1^3}{E_2 t_2^3} + \frac{E_2 t_2}{E_1 t_1}} (T-T_0) \tag{1}
\]

\[
Z_{\text{max}} = \frac{3 \left( t_1 + t_2 \right) l^2}{t_2^2} \frac{(\alpha_2 - \alpha_1)}{4 + 6 \frac{t_1}{t_2} + 4 \frac{t_1^2}{t_2^2} + \frac{E_1 t_1^3}{E_2 t_2^3} + \frac{E_2 t_2}{E_1 t_1}} (T-T_0) \tag{2}
\]

4. THERMO-MECHANICAL MICRO-STRUCTURE DEVELOPMENT

4.1 Simple Device Optimization

The initial attempt to optimize the laser beam deflection read-out scheme is represented in figure 4. The starting micro-structure substrates (fig. 4 left) were 0.6 to 1.0 \( \mu \text{m} \) thick with 20 \( \mu \text{m} \) wide supporting legs. A focused gallium ion beam was used to directly micro-machine the optimized micro-structure, including the Oak Ridge National Laboratory (ORNL) logo on the device pad. For chemical adsorption the optimized device has the same size pad area as the original device, however the supporting legs have been substantially modified. The new legs have been reduced in width from the original 20 \( \mu \text{m} \) to less than 4 \( \mu \text{m} \), and they have been thinned from 0.6 \( \mu \text{m} \) to 0.4

Figure 4. Initial bi-material thermo-mechanical device optimization.
μm. The narrowing of the supporting structure not only makes for a more pliable device, but it also reduces the thermal conductance by substantially reducing the cross section for heat flow. Thus if equivalent heat is deposited on the two pads shown in figure 4, the device on the right will produce more signal due to the restriction of heat transfer. This type of relatively simple uni-legged structure was used to take the TNT data shown earlier in figure 2. As the wavelength region from 2.5 to 14.5 μm was scanned across the pad of the device in figure 4, the bi-material micro-structure deflected when the adsorbed monolayer of TNT molecules absorbed the incoming photons and heated the pad. At wavelengths which the TNT did not heavily absorb, the device rapidly cooled and straightened out, producing less of a deflection signal. This thermally induced deflection as a function of wavelength is the CalSpec spectrum shown in figure 2.

4.2 Novel Device Architectures

It soon became obvious that the uni-legged devices were essentially optimized. A novel approach was required to further increase the thermal sensitivity of the micro-mechanical devices. This would contribute to the CalSpec effort by either decreasing the minimum detectable chemical concentration or allowing more rapid detection. The penta-lever design depicted in figure 5 contains a serpentine supporting leg structure that approximates the sensitivity of a device five times longer than the actual penta-lever. The basic configuration consists of a silicon substrate with a thickness of 1.0-1.2 μm. The supporting leg structure area is further thinned to 350-450 nm. The image on the left of figure 5 was the first penta-lever device developed. It is a simple bi-material design with the metal (gold, platinum, zinc, etc.) deposited uniformly on only one side of the silicon substrate to a thickness of 40-60 nm, depending on the silicon thickness. This represents a significant thermo-mechanical advantage over the previously discussed uni-levers structure. Not only can the legs be made effectively much longer, but the leg area compared to the uni-legged structure is larger providing additional photon absorption by the adsorbed surface chemistry. The device shown on the right of figure 5 is a more recent design that employs an alternating bi-material effect. Even though the device depicted is not a finished penta-lever, the alternating bi-material structure can be seen. This type of device is initially metalized on both sides of the silicon penta-lever structure. Then, using focused ion milling, the metal layer is selectively removed from legs 1, 3, and 5 from one side and legs 2 and 4 from the other side. This provides an alternating bi-material effect that further induces thermo-mechanical deflection for a given amount of temperature change.

4.3 Novel Device Modeling and Testing

As a result of the rather involved analytical solutions shown in equations 1 and 2 for a relatively simple bi-material device, the bulk of the recent work in understanding the behavior of the penta-lever structures has been numerical. SolidWorks and Cosmos software packages were used to create the mechanical model of the desired micro-structures and the thermo-mechanical analysis, respectively. Figure 6 illustrates the complex movement of the penta-lever structures. Since the read-out scheme employs laser beam reflection from the micro-structure pad, the alternating bi-material design is critical to the operation of the device. Figure 5. (Left) Serpentine pattern penta-lever design with simple bi-material structure. (Right) Advanced alternating leg bi-material design built around a penta-lever structure. Legs 1, 3, and 5 are configured as Si / Au and legs 2 and 4 are configured as Au / Si.

Figure 6. Complex thermal movement of an alternating bi-material penta-lever structure.
material approach has an additional advantage over previous configurations. Since the device pad is metal coated from both sides, there is only a deflection in the supporting leg structure. In previous approaches the pad would also warp from the bi-material construction and cause a lensing effect. This effect provided some measurement difficulties since it necessitated compensation for additional probe beam convergence or divergence. The comparison of the thermo-mechanical sensitivity between the two penta-structures is shown in figure 7. Experimentally we can see nearly a factor of three improvement in sensitivity for the alternating bi-material penta-lever structure compared to the simple bi-material penta-lever, both versions illustrated previously in figure 5. The numerical modeling predicted an almost order-of-magnitude improvement. We are yet to realize this much sensitivity improvement since the micro-machined structures are difficult to fabricate to the exact numerical modeling parameters. However this is the most sensitive thermo-mechanical micro-structure we have fabricated. Future direction for achieving greater sensitivity will focus on both material and micro-mechanical optimizations. The bi-material effect can be further optimized by selecting polymers instead of metals to use with the silicon substrates. Certain polymers have a factor of four greater coefficient of expansion compared to even zinc. The micro-mechanical structure can be taken to the next logical level to produce a seven legged hepta-lever device. The initial untested version of this micro-structure is shown in figure 8.

5. CONCLUSIONS

Micro-mechanical thermal sensing technology has made tremendous progress in recent years. The results presented in this paper demonstrate that substantially improved thermo-mechanical sensitivity devices can be fabricated for micro-calorimetric spectroscopy. Thus the extremely small detection thresholds reported previously can be substantially improved. The development has progressed through the initial uni-lever, tri-lever, simple bi-material penta-lever, and finally the alternating bi-material penta-lever. At each step significant thermo-mechanical sensitivity improvements were realized. Additional sensitivity improvements are possible by both material and structural optimizations. The bi-material effect can be enhanced by the use of certain polymers, instead of metals, that have expansion coefficients four times greater than even zinc. Additional structural modifications such as the yet untested hepta-lever also promise additional performance benefits.

6. ACKNOWLEDGMENTS

This work was supported by the Laboratory Director's Research and Development Program of Oak Ridge National Laboratory. Oak Ridge National Laboratory is operated for the U.S. Department of Energy by Lockheed Martin Energy Research Corporation under contract DE-AC05-96OR22464.

7. REFERENCES