Monitoring volatiles and flammable gases without electronics

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ABSTRACT

A sensor that integrates detection, transduction and display of the signal is presented in this work. The device contains an optical grating embed in thin films of elastomer (PDMS). The polymeric elastomer interacts with hydrocarbon gases and volatile organic compounds producing a molecular and conformational change. That change alters an optical grating embed in the polymer. This deconformation is detected as a change in display wavelength or color and can be accurately measured with a reflectometer. When exposed to different molecules or concentrations a corresponding color is easily detected by eye.

Keywords: hydrocarbon, gas, volatile, sensor, grating, reflection, color.

1 INTRODUCTION

A typical sensor design includes a detector, a transducer and a display. The detector is engineered to accurately interact with the molecule of interest or analyte. These interactions at the nanoscale are transduced to changes in the bulk properties of the material that can be measured in different ways. Gas sensors and flammable sensors operate in the same manner, a signal is generated (usually by burning the gas), the signal is transduced (semiconductor) and displayed on a screen or as an alarm. In this work, a sensor is designed for integrating the three components of a sensor into one: a display device with embed detector and transducer.

This new sensor comprises an optical grating embed in a sensitive polymer; when a molecule interacts with the polymer, the polymer experiences changes in properties, such as, refractive index or swelling state. These properties are also shared with the grating, integrating detector and transducer. Since the optical changes can be seen with the naked eye as a change in coloration or shape of the reflected image, the display capabilities are also integrated within.

The optical grating is a Bragg diffraction grating recorded with a laser (i.e. a volume hologram) using a mirror or a reflective surface to generate interfering standing waves. The photonic effect produced by the grating can be analyzed mathematically, as well as the molecular interactions between the polymer and the gases or volatile compounds. The sensor material is selected to interact specifically with such molecules. An easily available elastomer (PDMS) is used to contain the gratings allowing simple fabrication and durability. Similarities in cohesive energy densities, related to the intermolecular interactions, are a direct indicative of the level of response and affinity of the elastomer for different molecules. Molecules known to interact with PDMS are hydrocarbon gases, alcohols, ketones and other volatile compounds. The response signal is measured as a change in wavelength (or coloration) against concentrations or type of molecule. The chemical properties of PDMS have been studied broadly, so that an understanding of the chemical mechanisms involved in the sensing can be comfortably explained. In terms of affinity or solubility, alike molecules to PDMS would present a higher response. The capabilities of the sensor make it suitable for work in dangerous environments with enriched concentrations of those molecules. Changes in wavelength can be seen and interpreted by direct observation from a short or long distance without the need of electronic devices. Furthermore, the elastomer is highly resistant to corrosion, inert, castable, and water does not interfere with its performance [4].

2 THEORETICAL FRAME

The recorded grating is arranged according to the mirror or reflected surface used and will be spaced by half of the wavelength of the laser radiation. These recordings will contain all the information required to reconstruct the reflected image in three dimensions stored in the periodic grating [3]. Periodic structures at that scale cause a photonic effect of filtering white light, allowing only certain wavelengths to be reflected [7, 8]. Upon illumination with white light, the wavelength with the maximum reflectivity will be displayed at certain angles from the source [1–3,6]. This conditions are satisfied when:

$$\cos\theta = K/2nk_0 \tag{1}$$

where,

$$K = 2\pi/\Lambda \tag{2}$$

$$k_0 = 2\pi/\lambda \tag{3}$$

K is a grating vector, θ is the angle of incidence, n the refractive index of the medium, Λ the grating spacing and k_0 determined as the periodicity vector for a wavelength with the maximum reflectivity, simplifying,

$$\cos\theta = \lambda/2n\Lambda \quad (4)$$

With no significant changes in refractive index and invariable angles of incidence, a change in Λ would explain any change in λ and viceversa.

3 MATERIALS AND METHODS

Poly(dimethylsiloxane) was purchased from Dow Corning, UK. All reactants were analytical grade, purchased from Sigma-Aldrich. Gas cylinders from CKGases (99.9%), UK. Upon formation of thin PDMS films of approximately 20 μm on glass slides, a solution of silver pentafluoropropianate (Ag-PFP) in tetrahydrofuran (THF) and a solution of hydroquinone (HQ) in THF were perfused through the membrane from the surface. This process is a diffusion mediated process in which the rate and distance of perfusion of the silver salts and reducing agent (HQ) will depend upon the solvent and its affinity for PDMS. It was found that letting the solvent evaporate on top of the films using a 0.1M solution of HQ and a 0.2M solution of Ag-PFP was ideal for the formation of metallic-silver nano-particles beneath the surface. These nano-particles where, then, ablated with laser radiation to form the fringe structures after being ablated. A high energy Nd:YAG pulsed laser (532nm) with dichroic mirrors was used for this procedure. A portion of the film containing the grating was sealed in a gas flow cell for spectrophotometric analysis with an Avantes spectrophotometer. Electron microscopy analysis was done using a JEOL5800 equipped with a UTW x-ray scatter detector and a JEOL200CX electron microscopes. The samples were mounted on an aluminum support and coated with a thin layer of Pt for SEM, for TEM fine cross sections of the film were placed on Cu clip grids. The mounted sample in the cuvette holder was photographed with a Canon 400D digital SLR camera. The exposure to gas was performed by pumping the gas or vapor at 6mL/s flow rate.

4 RESULTS AND DISCUSSION

Response times for gases were ∼5s for a range of concentrations from 0% to 100%. A maximum wavelength shift was found for each concentration and type of gas, an example is shown in Figure1A. The reflected wavelength of the hologram shifts from its original reflected wavelength when exposed to the hydrocarbon gas. When washed thoroughly with an air flow the response returns to its original value this reversible process can be continuously repeated. The wavelength change and its associated coloration can be appreciated on the

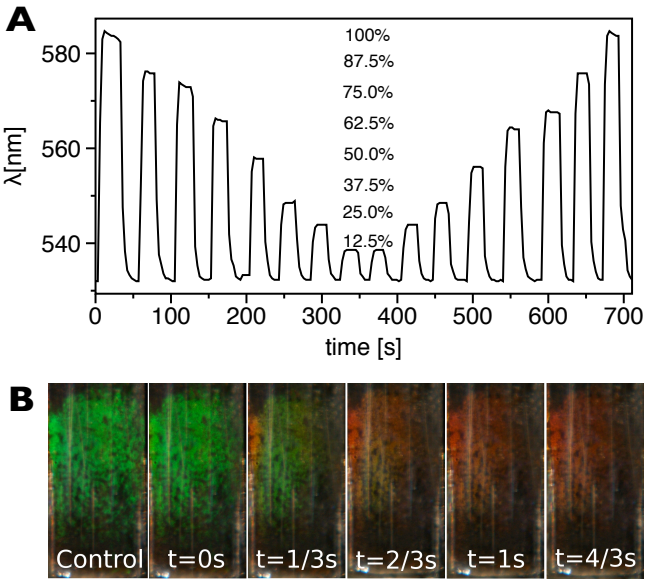

Figure 1: Reflected wavelength from grating when exposed to an analyte. A) Typical response to a gaseous hydrocarbon, inlet butylene at different concentrations (% v/v) and flushed with air, continuously recorded. B) Continuos photographing of film surface when exposed to acetone vapor for every third of a second.

example in Figure1B. This change is a fast transition from green to red through orange and yellow colors. The figure shows how acetone vapor produces a maximum shift in less than 2s. As only illumination with white light and an observer are required to obtain sensor information, the electronics can be left aside and are only required for more accurate measurements. The observer not only can be a human operator but also register information from the distance if the monitoring device is within its visual range.

The effect of the solubility of the PDMS results in an expansion of the polymer chains, therefore, in swelling of the films. It has been proven elsewhere [5] that a conformational change, driven by mechanical forces, leads to a change in the spacing Λ in equation 4. Here, a conformational change driven by chemical intermolecular interactions results in a change in Λ; therefore, a change in the reflected wavelength λ. It was also found that temperature affects the replay wavelength resulting in a small increase at low temperatures and decrease when the temperature was raised.

Electron microscopy analysis showed that the silver salts were successfully reduced and transformed into metallic nanoparticles. Figure2A shows a backscattered x-ray spectrum obtained from the sample during the SEM analysis. The scattered x-ray energy peaks correspond to the Si, C and O from the silicon elastomer and the Al and Pt peaks from the Aluminum sample holder and Platinum coating respectively. Moreover, Ag x-ray

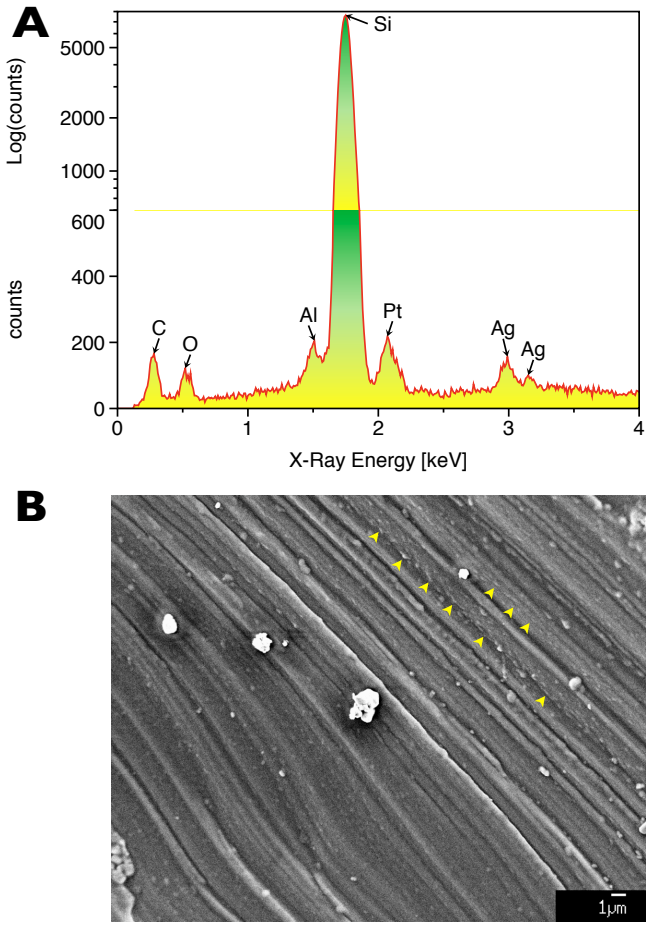

Figure 2: Scanning electron microscopy. A) Scattered x-ray counts for different x-ray energies in keV, peaks labeled with corresponding element. B) SEM micrograph showing silver nano-particles as protuberances on a cross-section of the grating, scale bar is 1μm.

energy count peaks were also detected from to the silver nanoparticles. The scale was fixed for values larger than 600. In Figure2B, the formed silver grains can be seen from a PDMS film cross-section marked by the yellow arrows. PDMS was 'charging' when bombarded with electrons, thus, imaging was a challenge. However, TEM analysis allowed to determine the size distribution of the silver nanoparticles in the film as discussed below.

The plot in Figure3 is a plot of the total number of particle counts (bars) against particle size in nanometers. The probability graph is also included, together with some statistical parameters. It was found that the particles have an average size of 19nm with higher count for smaller particles. Perhaps the resolution of the microscope wasn't enough to observe smaller particles or a larger sample is required. The graph shows small counts for particles bigger than 50nm; presumably the particle size distribution changed after ablation.

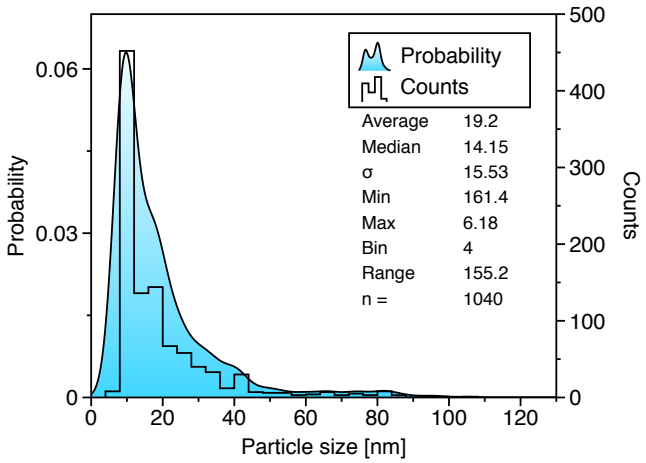

Figure 3: Particle size distribution by TEM analysis. Individual counts in bars, and probability shadowed curved, the mean size falls between 10nm and 20nm with an average of 19.2nm.

5 CONCLUSIONS

It was shown that monitoring flammable gases or volatile compounds using a device that does not need electronic dependent attachments is possible. The device is fabricated using an easily available elastomer (PDMS) that can accurately measure and detect a span of concentrations of a hydrocarbon gas without interference of water or water vapor, due to its chemical nature. The changes can be observed as a wavelength change by eye. The device can be interrogated from the distance upon illumination with white light. Organic vapors can also be monitored as a change in coloration. As the affinity for the analytes of the monitoring device depends on the type of material, other devices can be conceived by selecting materials with affinity for certain molecules of interest, thus, new sensing platforms that do not require electronics to be observed can be fabricated.

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