Xsense: Using nanotechnology to combine detection methods for high sensitivity handheld explosives detectors

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ABSTRACT

In an effort to produce a handheld explosives sensor the Xsense project has been initiated at the Technical University of Denmark in collaboration with a number of partners. Using micro- and nano technological approaches it will be attempted to integrate four detection principles into a single device. At the end of the project, the consortium aims at having delivered a sensor platform consisting of four independent detector principles capable of detecting concentrations of TNT at sub parts-per-billion (ppb) concentrations and with a false positive rate less than 1 parts-per-thousand. The specificity, sensitivity and reliability are ensured by the use of clever data processing , surface functionalisation and nanostructured sensors and sensor surfaces.

Keywords: Explosives detection, Surface enhanced Raman scattering spectroscopy, colorimetry, calorimetry, cantilever based sensor, TNT, DNT, data fusion

1. INTRODUCTION

In military and commercial fields there is an increasing demand for fast, portable, reliable, selective and sensitive detection methods for explosives and explosive related illicit materials. Major areas of applications for explosives sensors include: anti-terrorism (screening luggage, packages, people and mass transit systems), demining (clearance of mines and unexploded ordnance (UXO) in contaminated war zones) and in the field of environmental monitoring of hazardous compounds (f.ex. trinitrotoluene (TNT) can easily enter the groundwater and is classified as toxic to all life forms in concentrations above 2 ng/L).

Today, explosives are mainly detected by trained dogs. These dogs can detect explosives in concentrations as low as parts per trillion (ppt) and are the most effective detection principle currently in use. However, the sniffing dog has some limitations. Dogs are expensive to train and maintain. Furthermore dogs require an equally skilled handler whose training is also expensive and time consuming. Dogs can only work for a limited amount of hours and have behavioural and mood variations. Also, dogs often need retraining and/or time for acclimatisation when moved to a new environment.

In an attempt to address some of these issues the Danish Agency for Science and Technology's, Program Commission on Nanoscience Biotechnology and IT (NABIIT) has issued a € 3.850.000 grant to fund the Xsense [1] project which will be presented here. Xsense is projected to run for four years from mid 2008 to 2012. Four Ph.D. students, three post doctoral researchers in addition to four tenured professors distributed between the Technical University of Denmark and the University of Southern Denmark participate in the ongoing research. A close working relationship with the industrial partners Unisensor and SersTech has been secured from the project onset and these partners contribute with equipment and knowhow. The industrial goal is to provide Danish industry with new ideas for products and to assist them in further

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developing their current technologies in the sensor area. Furthermore, it is anticipated that new business ideas will emerge from the project, creating a technology platform for start-up companies.

The ultimate goal of the Xsense project is to realise a reliable, sensitive, portable and low-cost explosives detector. The project focuses on sensor fabrication and validation. The sensor system will be miniaturised and will therefore be highly suitable for the use in anti-terror efforts, border control, environmental monitoring and demining. At the end of the project, the consortium will have delivered a sensor platform consisting of four independent detector principles capable of detecting concentrations of TNT at sub parts-per-billion (ppb) concentrations and with a false positive rate less than 1 parts-per-thousand. The specificity, sensitivity and reliability are ensured by the use of clever data processing, surface functionalisation and nanostructured sensors and sensor surfaces. The inherent design qualities of the finished device should enable its use by personnel with minimal training thus giving these persons explosives detection capabilities otherwise only available to trained dog teams.

2. SENSOR TECHNOLOGIES

In the future development of sensor based explosives detectors we find that the key challenges to address are reliability, selectivity, stability and cost. Our hypothesis is that only by combing several independent and sensitive measuring principles can reliability be improved.

The scientific goal is to continue the development of miniaturised sensors in order to achieve sensitivity towards explosives (TNT is the major test molecule) of 1 ppb. The sensitivity will be optimized by a concentrated effort in data processing (reducing noise and pattern recognition), nano patterned and functionalised sensor surfaces, and the development and use of a sample pre-concentrator. Secondly, the goal is to improve the reliability of the explosives detection significantly by establishing a network of the independent sensors. Hereby a false positive rate less than 1 parts-per-thousand is anticipated.

The Xsense project develops four individual miniaturised sensor technologies (surface enhanced Raman scattering (SERS) spectroscopy, cantilever-based sensors, a calorimetric sensor and a colorimetric sensor) which each are able to detect explosives in concentrations of at least 1 ppm. Proof of concept has been confirmed for all four sensor technologies which have already been developed hence the ongoing effort will thus be in optimising the sensitivity. The project will allow us to compare the technologies in terms of sensitivity, reliability, ease of use and cost. Based on the analysis of the individual sensors and on input from the data processing activities a sensor network will be established. The idea is that the amount of false positives can be significantly reduced by increasing the number of independent sensing principles. The individual sensors as well as the network of sensors will be used for detection of explosives in air. Also, mixtures of explosives and influence of changes in humidity and temperature will be analysed.

2.1 Cantilever based sensing

In cantilever-based sensing, micrometer sized cantilevers with integrated piezoresistive or optical read-out are used to detect changes in surface stress. The top surface of a micro-cantilever is coated with a ‘detector’ layer which binds specific explosives. Upon binding of the molecules, the cantilever bends and the bending is detected electrically as a change in the resistance of the integrated piezoresistor or optically as a deflection of a laser light hitting the apex of the cantilever. This principle has been demonstrated to be able to detect for example PETN [2], RDX and TNT.[3] Recently, polymer cantilevers fabricated at DTU Nanotech were used for the detection of the nerve gas model DMMP [4]. Our challenge is to find selective coatings in order to bind the explosives and to minimise unspecific binding. Also, the read-out method needs to be robust and fast. Currently we are mainly investigating cantilevers for optical read-out and methods of packaging the cantilevers into a solid support structure [5]. An example of an array of polymer cantilevers placed in polymer housing is shown in figure 1. The cantilever bending will be read-out using the pick-up head from a DVD [6].

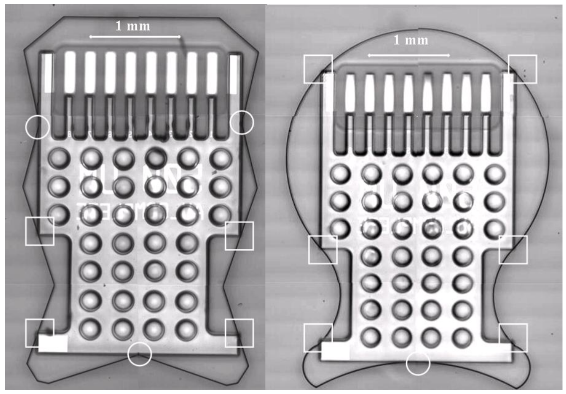

Figure 1: Top view optical microscope images of two footprint configurations for the clamping of cantilever chips. They integrate both edge-corner (round markers) and corner-edge (square markers) clamping points. Using these structures fabricated in polymer and Pyrex, the cantilever chips can be easily placed on a platform for read-out and sample handling.

2.2 Micro calorimetry

In micro-calorimetric measurements a heater element is placed on a micrometer sized bridge. The bridge furthermore contains a resistor, which dramatically changes its resistance when heated. In this way it is possible to perform local calorimetry, following for example the phase transition of materials (endothermic reactions). It has been demonstrated that this method can be used to distinguish TNT, DNT and EDX [7]. Alternatively, by rapid heating of the structure, deflagration of explosives might be initiated. Deflagration will cause a significant heat development (exothermic reaction). A schematic drawing of the chip as well as an example of a DNT coated bridge is shown in figure 2. Currently the explosives are passively adsorbed on the surface; however a surface functionalisation for improved specificity would be ideal. Also, catalysts might be placed on the heater element to cause a stronger deflagration upon rapid heating. This work occurs in collaboration with researchers from Oakridge National Laboratory, USA.

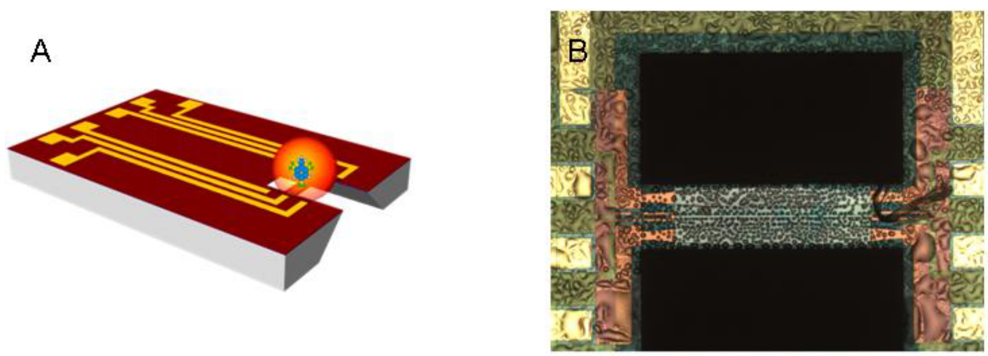

Figure 2. A) Graphic illustration of the sensing principle. Explosives attached to the micrometer sized bridge structure will deflagrate as the temperature of the bridge is rapidly increased using integrated heater elements. The resulting temperature increase as a function of time is used to map the presence of different explosives. B) Optical microscope image (top view) of bridge structure with evaporated DNT on top. The DNT forms a uniform coating of small droplets.

2.3 Raman spectroscopy

In Raman spectroscopy it is possible to identify a molecule by mapping its vibrational states. The molecule of interest is illuminated with laser light, which is scattered by the molecule. Part of the scattered laser light has been modified by the vibrational states of the molecule i.e. has undergone a shift in frequency. The substance can be identified by collecting the scattered laser light and analyzing the various shifts in frequency originating from the different vibrational states. We have developed a maskless fabrication process shown schematically in figure 3 in order to generate Raman enhancing surfaces. A silicon wafer is etched by reactive ion etching. The etch process is tuned such that it results in micromasking of the surface which is then used to define small and highly reproducible nanopillars on a full wafer surface.

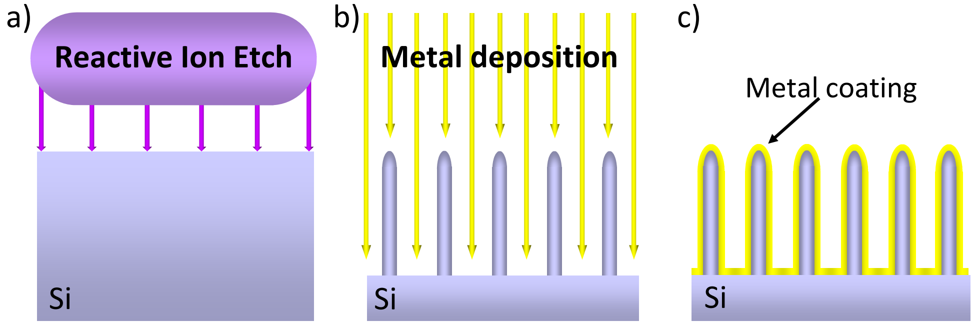

Figure 3. Schematic of the fabrication process. a) A blank silicon wafer is structured by maskless reactive ion etching to form free standing nanopillars. b) The pillars are coated with metal c) The resulting structure are free standing metal coated nanopillars with rough surfaces.

Recently, nano-structured surfaces have been developed that enhance the Raman cross section of certain molecules by 6-10 orders of magnitude, see Figure 4. The signal enhancement allows for a miniaturized detection system using chip-based micro spectrometers (supplied by SersTech) and cost efficient CCD elements.

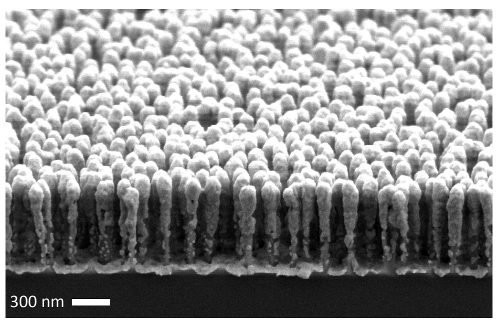

Figure 4: Scanning electron microscope image of nanostructured silicon surface optimised for enhancing the Raman effect. The silicon surfaces are coated with 50-400 nm thick layers of silver / gold. Note the large surface area.

2.4 Colorimetric array

Simple colorimetric sensor arrays have been shown useful in the detection, identification, and quantification of volatile organic compounds (VOC) in gas phase. Furthermore, they have been used to detect and differentiate mixtures of organic compounds dissolved in aqueous solutions. The sensor arrays are inexpensive, and can potentially be produced as single use disposables. The technology relies on an array of dyes immobilized on a solid support. Upon exposure to the analyte the dye array changes colour. Each dye is chosen as to react chemoselectively with analytes of interest. An example of colour changes upon exposure to DNT in gas phase is shown in figure 5. Different dies have been placed on a silica gel and a colour image has been taken before and after the DNT exposure. These images are used to create a difference map. The difference map is generated after a mathematical analysis of the colour changes. A difference map presents the difference in absolute value of RGB colours obtained from the absolute value of red, green or blue colour after the exposure of DNT minus the absolute value of red, green or blue colour before the exposure of DNT.

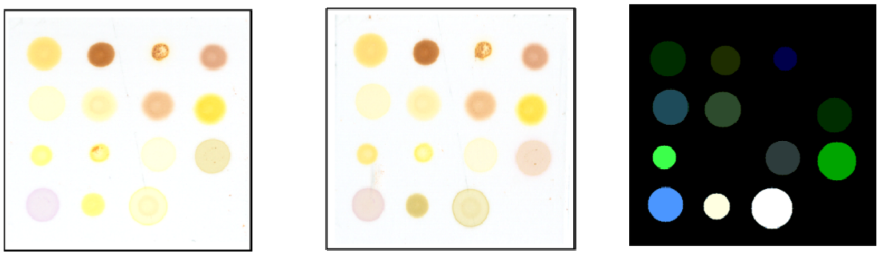

Figure 5: Colorimetric arrays before and after the exposure to DNT in gas phase. The two colour images are used to gerneta a diffence map which facilitates the signal interpreation significantly.

2.5 Signal processing

The optimal use of a network of sensors requires careful data processing. To obtain reliable and robust detection and quantification of explosives requires careful optimization of all steps in the data processing pipeline. The data processing pipeline includes: 1) Pre-processing: preparation/conditioning, noise removal and feature extraction of individual sensor data. 2) Data fusion: learning the optimal nonlinear combination of pre-processed data with the aim of predicting presence of explosives. The learning phase is done from sensor data sets assisted by reference measurements of explosive concentration. 3) Data presentation and evaluation: quantification of system's decision, uncertainty, robustness and reliability. We have extensive experience with such pipelines in diverse areas such as neuroimaging [8], skin cancer detection from Raman spectroscopy [9] and land mine detection [10].

3. CONCLUSION

Xsense aims at introducing micro- and nano technological approaches to the field of explosives detection. The concept of combining four sensor techniques in a hand held device coordinated by advanced mathematical signal processing appears to be a promising approach for low cost explosives detection and mine clearance.

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