Highly Sensitive and Selective Explosive Detector Based on Nanoporous Silicon Photonic Crystal Infiltrated with Emissive Organics

I.A. LEVITSKY

EMITECH INC. (WWW.emitechinc.com) is developing a porous silicon (PSi) microcavity (MC)-based fluorescent detector for explosives. It was initially funded by the Army Small Business Innovation Research Phase II contract (Figure 1). The sensory part of the device is composed of a nano-PSi photonic crystal with MC, infiltrated with fluorescent organics that are specific to target explosive vapors and particulates. It is important that the nanodevice structure provides an extremely large interfacial area between the sensory material and the analyte vapors leading to its highest sensitivity, which is critical for fast trace detection of low vapor pressure explosives. An important feature of the nanodevice is the real-time sampling system (integrated with sensory head) based on the proprietary thermal air-jet technology.

The capabilities and potential of the first portable prototype (Mark-I) and the second improved prototype (Mark-II) for explosive detection were successfully demonstrated in 2008 and 2009 by the Army representative. The Mark-II prototype is capable of detecting the cyclotrimethylenetrinitramine (RDX)/pentaerythritol tetranitrate (PETN)/trinitrotoluene (TNT) particulates and vapors in real-time mode using a proprietary sampling system based on an air-jet technique.

At the current stage, the nonoptimized prototype Mark-II is capable of detecting RDX and PETN particulates as low as 100 ng/cm^2. In addition, TNT can be detected within 5 s with a detection limit lower than 1 ppb (vapor trace detection) and ~2 ng/cm^2 (particulate detection). Depending upon the volatility of the trace explosives, the detection limit can be even lower at higher temperatures and with sample cooling.

The major advantages of the proposed detection system over existing chemosensors for explosives can be formulated as follows:

- Large interfacial area of nanoporous Si ranging from 200 to 800 m^2/cm^3, which provides numerous sites between PSi and analyte vapors. This should increase the sensitivity and response time.
- Dependence of the MC peak spectral position on the nature of the target analyte, resulting in high selectivity and minimum false alarms.
- The use of a real-time sampling system based on an air-jet technique, which is capable of covering a large interrogation area. This makes the device principally distinctive from the existing explosive detectors operating in swabbing mode (nonreal time) and using small interrogation area (point-type detection).
- Capability to employ multispectral format, e.g., simultaneously detect several MC peaks in the vis–near infrared (NIR) spectral range. This feature provides the basis for the sensor array implementation.

> An important feature of the nanodevice is the real-time sampling system (integrated with sensory head) based on our proprietary thermal air-jet technology.

(a) (b)

FIGURE 1 Images of the prototypes for explosive detection: (a) Mark-I and (b) Mark-II.

Digital Object Identifier 10.1109/MNANO.2010.938017

1932-4510/10/$26.00©2010IEEE

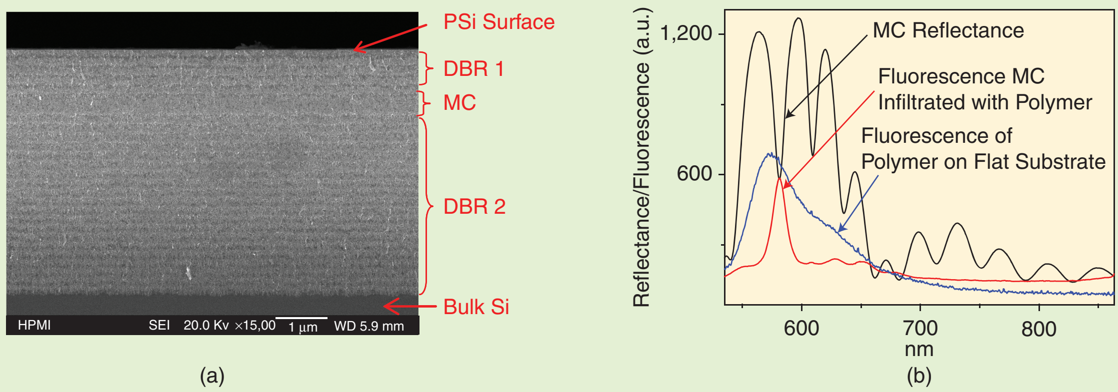

FIGURE 2 (a) Cross-sectional scanning electron microscope image of a DBR1/MC/DBR2 structure (MC) (b) Fluorescent broadband of a polymer spuncast on a flat substrate (blue) and narrow fluorescence peak of MC infiltrated with the same polymer (red). MC reflectance spectrum is shown for comparison (black). DBR: distributed Bragg reflector. (Data from Emitech's laboratory.)

- Simple and cost-effective fabrication process (electrochemical anodization of Si and MC impregnation/coating with the organics) that does not require high vacuum deposition.

Thus, this new concept should provide the development and testing of novel nanocomposite-based optochemical detectors with superior sensing properties for fast real-time, standoff detection and identification of explosive materials.

MC resonator (interference optical filter or photonic crystal), which is composed of alternating silicon layers with high and low porosity (Figure 2), is very attractive for optical sensing because of its sharp peak(s) [full-width at half-maximum (FWHM) ~ 10 nm] in the vis-NIR spectral range. The pore size is varied in the range of 5–20 nm depending on the etching conditions and Si doping. The spectral position of the MC resonance peak is sensitive to the refractive index of the vapor or the liquid inside the nanopores. Therefore, the different analytes entrapped inside the PSi MC induce a spectral shift of the resonance peak (reflectance/luminescence format) by providing an excellent transduction mechanism.

Introducing the sensory emissive polymer inside the MC nanoporous structure allows to simultaneously detect the spectral shift of the MC fluorescence peak [Figure 2(b)], with the fluorescence quenching upon analyte exposure. This provides a novel additional parameter that improves the analyte identification (discrimination in the case of explosive interferant). The unique combination of sensory organics and nanoporous photonic crystal provides high selectivity, which allows it to distinguish the different types of nitrocompounds, where these nitrocompounds are detected as explosives by conventional sensors inducing false alarms.

Figure 3 demonstrates the comparison between our detectors (Mark-I/Mark-II) and the conventional fluorescence-based detector in response to exposure of nitrotoluene, an interferant of TNT. A PSi MC infiltrated with a polymer shows a spectral shift and fluorescence quenching

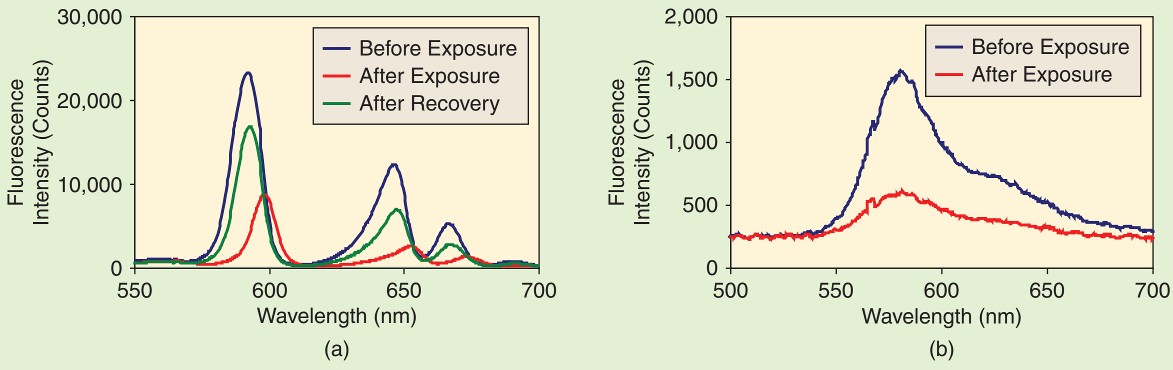

FIGURE 3 (a) Fluorescence quenching and spectral shift upon nitrotoluene exposure for PSi MC infiltrated with sensory fluorescence polymer and (b) for the same polymer deposited on flat Si upon nitrotoluene exposure. (Data from Emitech's laboratory.)

upon nitrotoluene exposure [Figure 3(a)]. On the contrary, a flat silicon wafer coated with a polymer [Figure 3(b)] shows quenching only and does not distinguish between nitrotoluene and TNT, which could likely result in false detection. Similar results can be obtained for the particulate mode.

The developed product has a strong commercial potential on the current market of portable explosive detectors. The proposed novel optical chemosensors are highly promising to be more sensitive and selective, lightweight, faster, and less expensive than other current standoff and man-portable detectors for explosives. The need for improvised explosive device (IED) detectors is growing exponentially. Homeland Security Research reports forecast the global counter IED market to reach US$23 billion from 2008–2018.

> Mark-II prototype is capable to detect the RDX/PETN/TNT particulates and vapors in real-time mode using our proprietary sampling system based on air-jet technique.

In addition to military applications, the proposed novel detecting system can be successfully employed for humanitarian demining, security of public places (air and seaports, checkpoints, subways, stadiums), and government objects, where there is a high risk of terrorist attacks. Also, because the detector can be tuned to other classes of chemicals, such a system will find many commercial applications in the chemical and biotechnology industries for real-time control in technological processes. To date, market analysis displays a highly growing interest in such low-cost and effective sensor devices.

ABOUT THE AUTHOR

I.A. Levitsky (ilevitsky@emitechinc.com) earned his Ph.D. degree from the Institute for Low Temperature Physics, Ukraine, in 1991. He has been the principal scientist at Emitech, Inc., in Fall River, Massachusetts, since 2002 and is adjunct assistant professor in the Department of Chemistry, the University of Rhode Island.