Fluorescent Gas Sensors Based on Nanoporous Optical Resonators (Microcavities) Infiltrated With Sensory Emissive Polymers

Pang-Leen Ong and Igor A. Levitsky

***Abstract*—In this contribution, we report fluorescent gas chemosensors for detection of nitroaromatic vapors and other classes of volatile organic compounds based on porous silicon (PSi) microcavity (MC) infiltrated with sensory emissive polymers. Such hybrid functional sensors have several advantages over traditional fluorescent chemosensors, where the sensory polymers are deposited on flat substrate. This includes a high interfacial area of nanoporous Si (high sensitivity), narrow fluorescent band due to photon confinement, dependence of the spectral peak position on nature of analyte (enhanced selectivity), and fast recovery time. We demonstrated that deep and uniform polymer infiltration is critical for effective gas sensing and investigated the experimental conditions required for preparation of high-quality hybrid sensors. In the case of deep infiltration, the broad polymer fluorescence (FWHM $\sim$ 100 nm) shows a narrowing to the resonance peak (FWHM $\sim$ 10 nm) with narrow intensity angle diagram. In addition, the potential of the sensor array platform and sensor recovery under ultrasound power is discussed.**

***Index Terms*—Chemical sensors, gas detectors, explosive detectors, nanostructured materials.**

I. Introduction

POROUS silicon (PSi) chemical and biological optical sensors have been intensively studied for the past decade because of the high surface area of PSi and the variety of optical transduction mechanisms upon exposure to different analytes. The sorption of the target molecules into the silicon pores modifies the refractive index and, consequently, the optical properties of PSi. Optical sensors based on Bragg mirrors, luminescent and reflective microcavities (MCs) have been reported in literature [1]–[7]. As distinct from biological PSi sensor with a high selectivity in aqueous medium [8], gaseous chemical sensors as a rule demonstrate a lack of specificity to target analytes. Furthermore, most of the tested organic gaseous analytes (alcohols, saturated hydrocarbons, chloromethanes) must display high vapor pressures ($\sim 10 - 100 \times 10^{-5}$ mm Hg) in order for the change in the reflectance or luminescence of PSi structures to be detected. The detection of vapors with low vapor pressure ($\sim 10^{-5}$ mm Hg and lower), is a challenge by these methods since nonspecific sorption coupled with low analyte concentration in the pores is not sufficient to uniquely alter the optical properties of PSi.

It is known that some conjugated polymers exhibit a high sensitivity to nitroaromatic molecules resulting in strong quenching of their emission. Several types of conjugated polymers have been specially designed for effective sensing of nitroaromatic molecules (including TNT) with low pressure of saturated vapors [9], [10]. Later it was found that fluorescence of other conjugated polymers can also be effectively quenched by nitroaromatic vapors [11].

Thus, it is expected that entrapping these polymers inside PSi microcavity should significantly improve the sensor's efficiency due to specific binding of nitroaromatic molecules to the sensory polymers, high quantum fluorescence yield of the polymers (higher than PSi self-luminescence), amplification mechanism as a result of the energy migration [12], and the fine spectral patterning of the broad florescence band induced by the MC structure.

II. Experimental

The fabrication of PSi MCs is described elsewhere [13]. Briefly, they were prepared by anodic etching of p-type (100)-oriented Si wafers (resistivity $\sim$ 0.01 Ω-cm) in 15% solution of HF with ethanol. The microcavity structure consists of a Fabry–Perot resonator between two distributed Bragg reflectors (DBRs) fabricated from alternating layers of high and low porosity. Anodization was performed under a periodically changing current applied between a silicon wafer and a platinum electrode. In fabricated samples, the first DBR consists of 5 periods, while the second has 20 periods; each period contains two layers, high and low porosity. For most samples, the low and high porosity layers were fabricated at a current density of 6 $\mathrm{mA/cm^2}$ and 25 $\mathrm{mA/cm^2}$, respectively. The MCs were oxidized at 850 °C under oxygen flow for 20 min. MC was infiltrated with poly(2-methoxy-5-(2-ethylhexyloxy)-p-phenylenevinylene) (MEH-PPV) (MW = 139000) and polyfluorene (PFO) (MW = 40000 − 120000) soluble in chloroform using spin cast processing with a defined delay time. The delay time (before spin cast) of approximately 20 s was necessary for solvent infiltration inside the nanoporous structure governed by capillary forces.

Manuscript received February 18, 2011; accepted April 25, 2011. Date of publication May 05, 2011; date of current version October 26, 2011. This work was supported by the U.S. Army Research Grant. This is an expanded paper from the IEEE SENSORS 2010 Conference. The associate editor coordinating the review of this paper and approving it for publication was Prof. Massood Atashbar.

The authors are with Emitech, Inc., Fall River, MA 02720 USA (e-mail: ilevitsky@emitechinc.com).

Color versions of one or more of the figures in this paper are available online at http://ieeexplore.ieee.org.

Digital Object Identifier 10.1109/JSEN.2011.2150213

1530-437X/$26.00 © 2011 IEEE

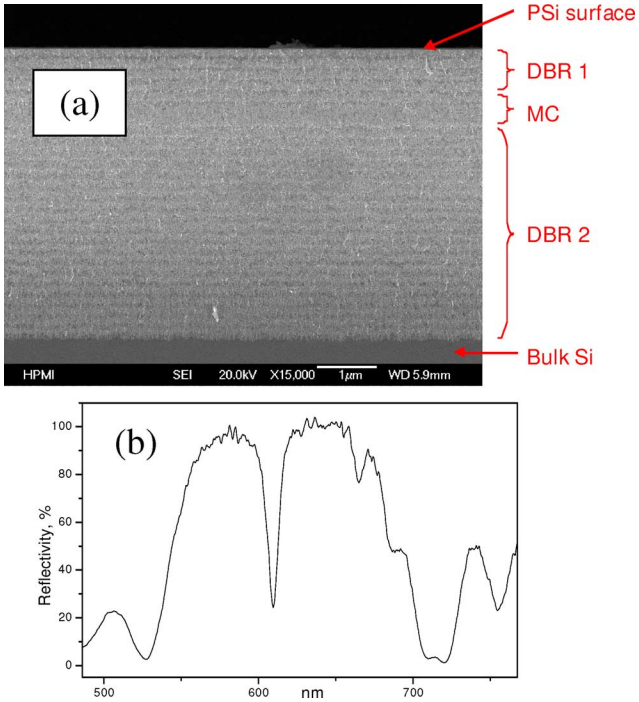

Fig. 1. (a) Cross-sectional SEM image of a DBR1/MC/DBR2 structure (microcavity) and (b) the corresponding reflectivity spectrum. DBR stand for Distributed Bragg Reflector.

The reflectance and fluorescent spectra were measured with an Ocean Optics spectrometer coupled with an optical fiber positioned normal to the sample surface. Fluorescence was excited by blue LED (365 nm, 5 mW) through the fiber directed at 30° towards the sample surface.

The samples were tested inside a custom designed flow cell operating under flow rate in the range of 100–500 cc/min. In the special case where ultrasound was applied, the samples were placed in a test chamber (30 ml) equipped with a flow controller to regulate the humidity or vacuum level. An ultrasound transducer (NDT Olympus A126S-RM, Resonance Frequency – 5 MHz, FWHM – 4 MHz, Max. Power –125 mW) working under AC sinusoidal voltage from a functional generator was coupled with the back side of MC through silicon grease. The thin silicon grease layer was applied on the back side of the Si wafer, followed by firmly pressing to the transducer surface.

III. Results and Discussions

Fig. 1 shows the cross-sectional scanning electron microscope (SEM) image of DBR/MC/DBR structure (in the following MC) prepared by electrochemical anodization and the corresponding reflectance spectrum. Oxidation of MC is required for polymer solution wetting, resonance peak stabilization, and high fluorescence yield of infiltrated polymer. Without the relatively thick silicon oxide layer, the fluorescence is substantially quenched. Porous branch-like structure for each layer is constituted from interconnected nanopores which size ($\sim 5-15$ nm) depends on anodization current [individual nanopores are not seen in Fig. 1(a)].

Deep polymer infiltration results in narrowing of the broad polymer fluorescence to the resonance peak, matching the MC peak in the reflectance spectrum (Fig. 2). The intensity-angle diagram of the peak is elongated and significantly narrower than polymer deposited on flat substrate (not shown here), which is an indication of the photon confinement in MC structure.

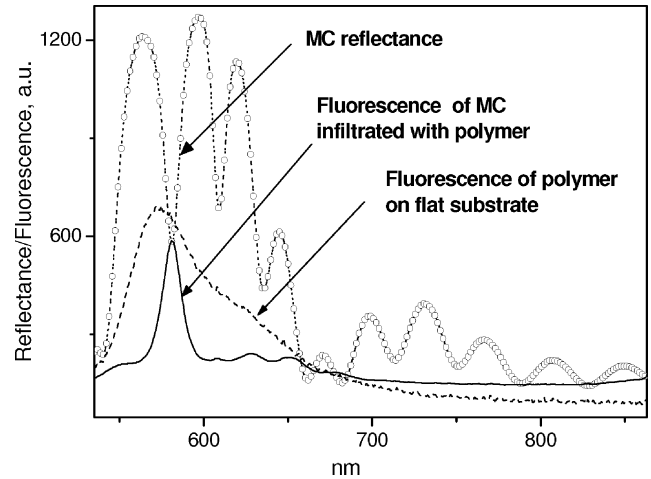

Fig. 2. MC reflectance, fluorescence of MC with infiltrated MEH-PPV and fluorescence of MEH-PPV on flat substrate.

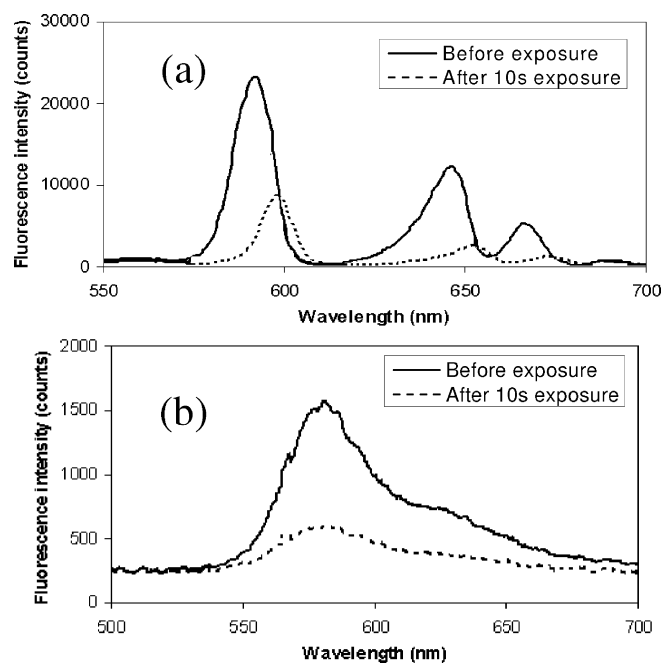

Fig. 3. Response of (a) MC infiltrated with polymer and (b) polymer deposited on flat substrate (right) upon 10 s exposure to nitrotoluene vapors.

Fig. 3(a) shows the fluorescence quenching and the simultaneous spectral shift of MC fluorescence peak upon exposure to nitrotoluene saturated vapors. At the same conditions, the polymer deposited on flat substrate exhibits only fluorescence quenching [Fig. 3(b)]. Thus, the MC fluorescent peak provides an additional parameter for recognition, namely, the dependence of fluorescence quenching on the detection wavelength (spectral shift). This feature can be very useful for discrimination of nitroaromatic interferants from nitroaromatic explosives. In addition, we found that fluorescence of MC peak is also sensitive to other groups of volatile organic compounds (ethanol,

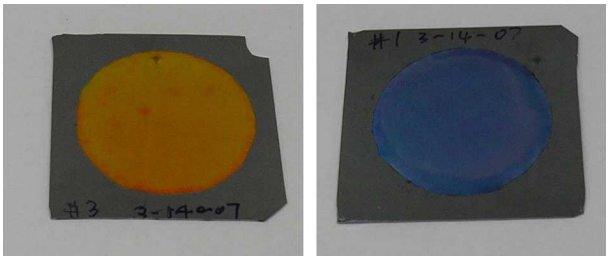

Fig. 4. Photo images of MCs on Si wafer tuned to yellow (left) and blue (right) part of visible spectrum.

chloroform, acetone, etc.), demonstrating a unique response for each vapors in the intensity-spectral domain. As most nitroexplosives (TNT, RDX, PETN) exhibit a very low vapor pressure (ppb-ppt range), their exposure is not sufficient to change the refractive index of MC and induce a significant spectral shift of resonance peak (e.g., nitrotoluene vapors). However, interaction of their molecules with sensory conjugated polymers affects the polymer emission resulting in a sizable fluorescence quenching. Thus, a simple recognition algorithm can be introduced in the detection scheme to minimize false positives: any fluorescence quenching (or enhancement) accompanied with spectral shifts should be indicative of the nitroexplosive interferant, while quenching only (no spectral shift) denotes only the presence of explosives.

To further increase the selectivity of the detection system, a sensor array format can be employed. This suggests the existence of several MCs tuned to different spectral range and infiltrated with different sensory emissive polymers. Fortunately, electrochemical anodization allows the fabrication of MCs with broad stop band and narrow resonance peak for the whole visible and NIR spectrum. Fig. 4 shows the photo images of two MCs tuned to blue and yellow part of the visible spectrum. "Yellow" MC with resonance peak centered at 580–600 nm is infiltrated with MEH-PPV polymer [Figs. 2, 3(a)], while "blue" MC with resonance peak at 465 nm is infiltrated with polyfluorene (PFO) polymer, which has blue fluorescence. The fluorescence signal response (spectral and time traces) of MC/MEH-PPV and MC/PFO are shown in Fig. 5. Interestingly, PFO quenching by nitrotoluene is a significantly fast reaction that the spectral shift of the resonance peak is not observed. By the same manner, more sensory elements can be designed forming the array distributed through the entire visible and NIR spectral range.

An important aspect for the chemical sensor performance is the recovery of the sensory material after analyte exposure. Usually, for this goal, heating and purging with clean air/inert gas is necessary to desorb analyte molecules from the sensor surface. Nevertheless, in many cases, the recovery takes a long enough time to provide multiple detection cycles. Recently, we found [14] that ultrasound facilitate desorption of water and organic vapors from the porous Si monolayer and MCs. The measurements were performed in reflectance format only using bare porous structures. The similar effect has been observed for MC infiltrated with MEH-PPV when the fluorescence signal was detected. If the full recovery (intensity and spectral shift) upon 10 s

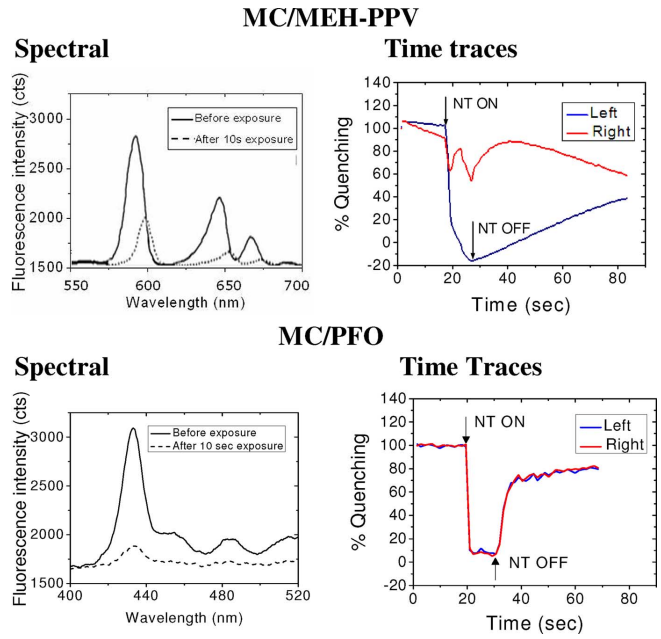

Fig. 5. Comparison of spectral responses and time traces upon 10 second exposure to nitrotoluene vapors for MC infiltrated with MEH-PPV and MC infiltrated with PFO. Left and right time traces corresponds to the time dependence of the half of the intensity of MC fluorescence peak taken at short- (left) and long (right)-wavelengths peak shoulders.

exposure of nitrotoluene saturated vapors usually takes up to 5 min (MC heating and purging hardly improve recovery time), the application of ultrasound from the back side of Si wafer reduces recovery time by a factor of 3–4. Such improvement is consistent with results from study [14] for bare MC.

The developed approach can be applied for detection not only explosive vapors and their interferants but also for detection and identification of common volatile organic compounds. Fig. 6 demonstrates the time traces of MC peak upon exposure to chloroform, ethanol and acetone saturated vapors. These responses are very specific to each analyte and can be employed for identification of organic vapors and their blends in the array format with nonstatistical pattern recognition methods.

IV. Device Prototypes and Conclusion

In conclusion, the major advantages of the proposed detection approach can be formulated as follows.(i) Large interfacial area of microcavity, which provides numerous sites between sensory material and analyte vapors/particulates. (ii) Dependence of resonance peak spectral position on the nature of the target analyte resulting in high selectivity and minimal false positive alarms. (iii) Capability of employing a multispectral format, e.g., simultaneously detecting several peaks in the Vis – NIR spectral range. This feature provides the basis for sensor array implementation: (iv) Simple and cost effective fabrication process (electrochemical anodization of Si and porous Si infiltration with the organics) that does not require high vacuum deposition.

Currently, two prototypes for explosive detection based on the described approach have been built in Emitech's laboratory (Mark-X series). The Mark-II prototype is capable of de-

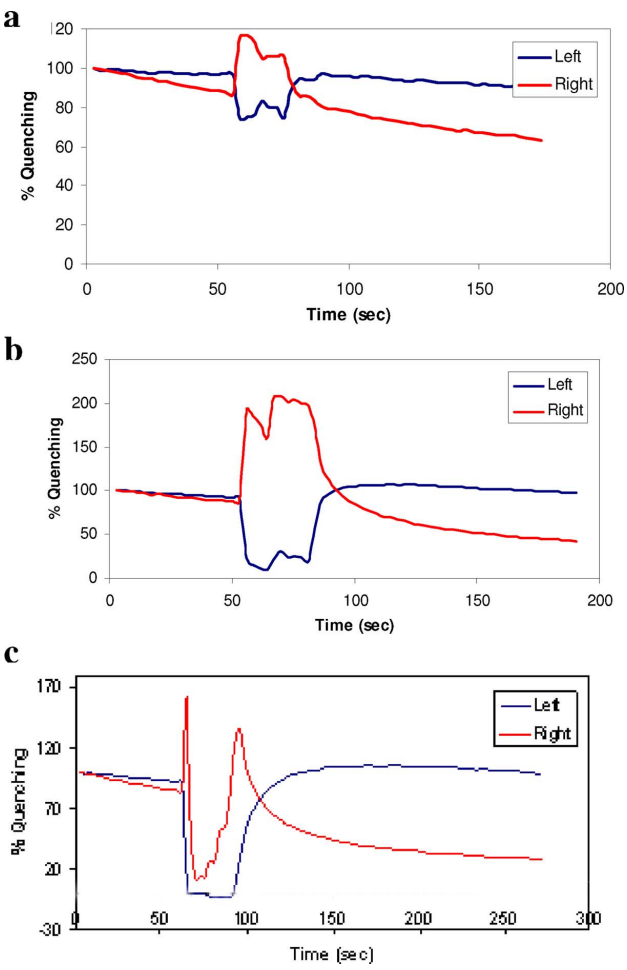

Fig. 6. Comparison of time traces upon 30 s exposure to (a) chloroform, (b) acetone, and (c) ethanol for MC infiltrated with MEH-PPV. Left and right time traces corresponds to the time dependence of the half of the intensity of MC fluorescence peak taken at short- (left) and long (right)-wavelengths peak shoulders.

tecting RDX/PETNT/TNT particulates and vapors in real time mode using our proprietary sampling system. Another feature of Mark-II prototype is the capability of the sensor to be mounted onto robotic vehicle and wireless communication with a remote terminal.

The use of the sampling system significantly improves the detector sensitivity, enabling real time detection of explosive particulates at $\mathrm{ng/cm^2}$ level. Such sampling approach enables prototype to attain fast response time (several seconds) and provides real-time, noncontact sampling for major explosives including TNT, RDX, and PETN. Thus, these features present substantial progress over other explosive detectors when the contact sampling is separated in time from the explosive detection (swabbing mode). At the current stage, Mark-II prototype is capable of detecting RDX and PETN particulates as low as 100 $\mathrm{ng/cm^2}$ in real-time mode. In addition, TNT can be detected within 5 s with a detection limit of less than 1 ppb (trace detection) and $\sim 20\ \mathrm{ng/cm^2}$ (particulates detection). Depending upon the volatility of the trace explosives, detection limit can be even lower at higher temperatures and with sample cooling.

The prototypes are equipped with a miniature optical spectrometer which allows detecting not only the change of the intensity of the fluorescence resonance peak, but also its spectral shift upon exposure of explosives. That provides a novel additional parameter which considerably reduces false positive alarm that could be beneficial in the design of next generation sensors for explosives detection.

Acknowledgment

The authors are thankful to BCO, Inc., for assistance in prototype development.

References

[1] P. A. Snow, E. K. Squire 1, P. S. J. Russell, and L. T. Canham, "Vapor sensing using the optical properties of porous silicon Bragg mirrors," *J. Appl. Phys.*, vol. 86, pp. 1781–1784, 1999.

[2] J. Saarinen, S. Weiss, P. Fauchet, and J. E. Sipe, "Optical sensor based on resonant porous silicon structures," *Opt. Exp.*, vol. 13, pp. 3754–3764, 2005.

[3] V. Mulloni and L. Pavesi, "Porous silicon microcavities as optical chemical sensors," *Appl. Phys. Lett.*, vol. 76, pp. 2523–2525, 2000.

[4] S. Chan, S. R. Horner, P. M. Fauchet, and B. L. Miller, "Identification of gram negative bacteria using nanoscale silicon microcavities," *J. Amer. Chem. Soc.*, vol. 123, pp. 11797–11798, 2001.

[5] V. S.-Y. Lin, K. Motesharei, K.-P. S. Dancil, M. J. Sailor, and M. R. Ghadiri, "A porous silicon-based optical interferometric biosensor," *Science*, vol. 278, pp. 840–843, 1997.

[6] C. Pacholski, M. Sartor, M. J. Sailor, F. Cunin, and G. M. Miskelly, "Biosensing using porous silicon double-layer interferometers: Reflective interferometric Fourier transform spectroscopy," *J. Amer. Chem. Soc.*, vol. 127, pp. 11636–11645, 2005.

[7] L. D. Stefano, I. Rendina, L. Moretti, S. Tundo, and A. M. Rossi, "Smart optical sensors for chemical substances based on porous silicon technology," *Appl. Opt.*, vol. 43, pp. 167–172, 2004.

[8] M. J. Sailor, "Color me sensitive: Amplification and discrimination in photonic silicon nanostructures," *ACS Nano*, vol. 1, pp. 248–252, 2007.

[9] J.-S. Yang and T. M. Swager, "Fluorescent porous polymer films as TNT chemosensors: Electronic and structural effects," *J. Amer. Chem. Soc.*, vol. 120, pp. 11864–11873, 1998.

[10] H. Sohn, M. J. Sailor, D. Magde, and W. C. Trogler, "Detection of nitroaromatic explosives based on photoluminescent polymers containing metalloles," *J. Amer. Chem. Soc.*, vol. 125, pp. 3821–3830, 2003.

[11] C.-P. Chang, C.-Y. Chao, J. H. Huang, A.-K. Li, C.-S. Hsu, M.-S. Lin, B. R. Hsieh, and A.-C. Su, "Fluorescent conjugated polymer films as TNT chemosensors," *Synthetic Metals*, vol. 144, pp. 297–301, 2004.

[12] I. A. Levitsky, J. Kim, and T. M. Swager, "Energy migration in a poly(phenylene ethynylene): Determination of interpolymer transport in anisotropic Langmuir–Blodgett films," *J. Amer. Chem. Soc.*, vol. 121, pp. 1466–1472, 1999.

[13] I. A. Levitsky, W. B. Euler, N. Tokranova, and A. Rose, "Fluorescent polymer porous silicon microcavity devices for explosives detection," *Appl. Phys. Lett.*, vol. 90, pp. 041904-1–041904-3, 2007.

[14] I. G. Kolobov, W. B. Euler, and I. A. Levitsky, "Optical humidity sensing and ultrasound effect for mesoporous silicon 1-D photonic crystals," *Appl. Opt.*, vol. 49, pp. 137–141, 2010.

Pang-Leen Ong received the B.S. and M.S. degrees in 2002 and 2004, and the Ph.D. degree in electrical engineering from the University of Kentucky, Lexington, KY, in 2008.

He is a Research Scientist for this project, has over eight years of experience in the field of semiconductor device physics, fabrication, electrical characterization, failure analysis, and reliability engineering. Prior to joining Emitech, Inc., he was a Reliability Engineer at Qimonda AG. He is actively involved at

Emitech, Inc., in the development and evaluation of prototypes, and the implementation of uncooled, nano-scale infrared photodetectors for missile-seeking applications. His research interests include MOS device reliability, and the modeling, fabrication, and characterization of novel semiconductor devices such as carbon nanotube-based/semiconductor hybrid structures.

Igor A. Levitsky received the M.S. degree in physical optics from the Department of Physics, Kharkov State University, Kharkov, USSR, in 1979 and the Ph.D. degree in physics from the Institute for Low Temperature Physics and Engineering, Kharkov, USSR, in 1989.

He has over 20 years of experience in the technology development, experimental and theoretical study of physical/chemical properties of organic and composite materials including conjugated polymers, carbon nanotubes, organic-inorganic nanocomposite, liquid crystals, biopolymers, molecular aggregates and crystals. He has conducted research on a new class of nanostructured films of conjugated polymers, charge transfer complexes and liquid crystals (a promising new class of sensory materials for explosives) during his work at Massachusetts Institute of Technology (1997–1999). Also, he was directly involved in the development of fluorescence-based chemosensors for detection of land mines and IEDs. He was actively involved in the SBIR program during 1999–2001, when he worked as a Senior Scientist at the Altair Center, Shrewsbury, MA. Since March 2002, he has served as a Principal Scientist at Emitech, Inc., being a Principal Investigator of seven SBIR Phase I and two Phase II projects related to optochemical sensors to explosives, organic-inorganic nanocomposite solar sells, carbon nanotube-based IR detectors, and photomechanical actuators. Last year, he was PI of the Phase II project related to novel porous Si nanocomposite chemical sensors for IEDs detection. He is an adjunct faculty member of the Department of Chemistry, University of Rhode Island. He has more than 50 publications in peer reviewed journals and many presentations at U.S./International conferences. He is the coauthor of eight patents (three pending).

Dr. Levitsky is a member of the Material Research Society, Reviewer for *Advanced Functional Materials, Applied Physics Letters*, the *Journal of Luminescence*, the *Journal of Solid State Electronics*, *Langmuir*, and the *Journal of Applied Physics*. He is a member of editorial board of the *Journal Nanomedicine and Nanotechnology*.