Smart Dust: Sensors Derived From Photonic Crystals and Luminescent Quantum Dot Structures in Nanocrystalline Porous Si

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Nanocrystalline Porous Silicon Layers. Porous silicon is a nanocrystalline material that is generated by etching of bulk crystalline silicon in aqueous hydrofluoric acid (HF). It is of interest for its luminescence,[1] electroluminescence,[2] biolomedical, and sensor properties.[3] The open pore structure and large specific surface area (a few hundred m^2 per cm^3, corresponding to about a thousand times the surface of the polished silicon wafer) make porous Si a convenient material for sensitive detection of liquid and gaseous analytes. The ability to electrochemically tune the pore diameters[4] and to chemically modify the surface[5, 6] provides control over the size and type of molecules adsorbed. These properties have been exploited to develop PSi sensors for detection of toxic gases,[7, 8] solvents,[9-11] explosives,[12] DNA,[13, 14] and proteins.[4, 15, 16] The main techniques investigated to achieve signal transduction are capacitance,[17] resistance,[18] photoluminescence[19] and optical reflectivity.[20] Detection limits of at least a few ppb have been demonstrated for some of these.[3]

Luminescent Nanostructures in Silicon. Detection of analytes can be achieved by quenching of luminescence from the nanocrystallites that exist in porous Si matrices. Porous Si consists of an ensemble of interconnected nanometer-sized silicon crystallites, which can have dimensions small enough to exhibit quantum confinement effects. Carriers generated by UV excitation are confined in the silicon nanocrystallites.[21] The gap of the bulk silicon (1.1eV) is then increased by the confinement energy and visible photoluminescence (PL) is observed. Because of their high surface-to-volume ratio, quenching of photoluminescence from these nanoparticles can occur at very low analyte concentrations. Energy and charge transfer quenching mechanisms have provided the lowest detection limits for this mode of sensing.[9, 12, 22]

Chemical Sensors from Optical Interference. The determining physical parameter for the optical reflectivity sensor devices is the optical thickness of the films, which is the product of the refractive index (n) and the thickness (L). Binding of analyte in the pores changes n, leading to a sensitive transduction modality for a variety of analytes.

It is possible to fabricate more sophisticated optical devices from porous Si films. Pavesi and Mazzoleni[23] reported in 1995 the first P^+ type microcavity made entirely out of porous Si. Chemical sensing using Bragg mirrors of porous Si was first demonstrated by Snow and coworkers,[10] and recently Fauchet and coworkers demonstrated femtomolar-level detection of single-stranded DNA using a slightly more complicated optical microcavity structure that had been modified with the complementary-DNA strand.[13]

"Smart Dust" Chemical Sensors. Silicon smart dust particles are encoded by generating layers of nanometer-scale porous films in the silicon wafer using a programmed electrochemical etch. They are then released from the silicon wafer by an electropolishing pulse and broken into small particles by an ultrasonic treatment. The layered nanostructure imparts unique optical and sensing properties to the particles.

Si Smart dust can be used as a remote sensor for pollutants and toxic chemicals. For example, small particles of nanoencoded microporous Si have been used to detect chemicals by measurement of the intensity of reflected light from a remote laser probe. The intensity and wavelength of reflected light is determined in part by the refractive index of the porous nanostructure, which can be modified by adsorption of vapors within the porous matrix. These particles can be probed using small lasers and observed at distances of up to 25 m in bright sunlight. Irreversible detection and reversible sensing modes for explosives, nerve warfare agents, volatile organic compounds (VOCs), and various biochemicals have been demonstrated.

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