

Properties of Fluorescent Polymers Used in a Porous Silicon Explosives Sensor

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Advantages of Porous Structures

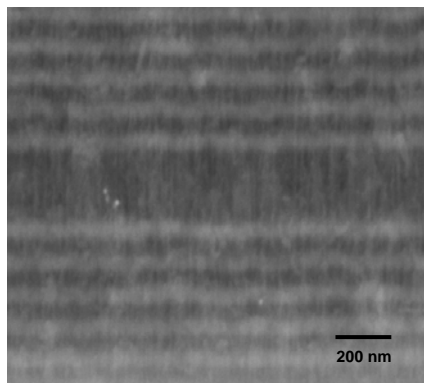
- Huge interface area: the surface area of porous Si ranges from 200 to 800 m² /cm³, which will dramatically increase sensitivity.
- Sharp fluorescence peaks: photon confinement in a microcavity gives peak/hole widths of 5 – 10 nm compared to conventional optodes based on organic fluorophores where band widths are 100 – 150 nm.
- Freestanding membranes: the porous Si microcavity can be fabricated as a freestanding film, which will facilitate the filling to pores with polymers/dyes and access to the analyte vapors.
- Simple and cost effective fabrication process: electrochemical anodization of Si and microcavity impregnation/coating with the organics does not require high vacuum deposition, photolithography, or clean room facilities.

Microcavity Structure

36 % porosity, 55 nm

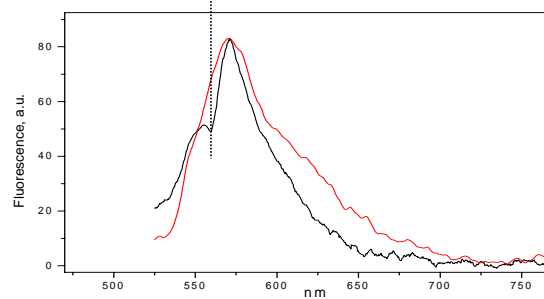
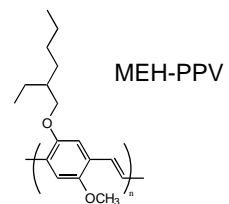
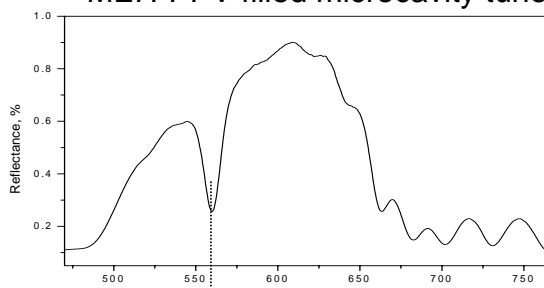
59 % porosity, 95 nm

36 % porosity, 210 nm



Side View of Fractured Sample

MEH-PPV filled microcavity tuned to 560 nm

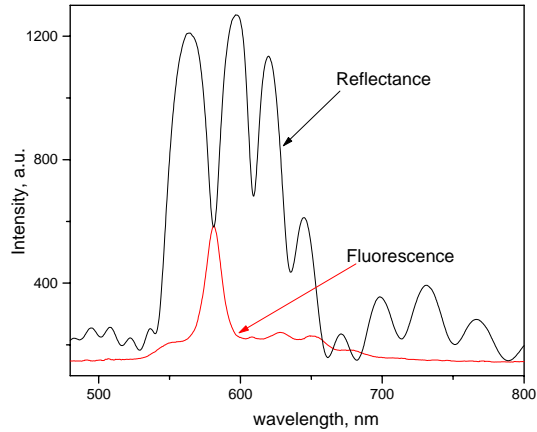


Red: Emission spectrum on a flat silicon surface

Black: Emission spectrum from a microcavity

Top layer has small pores

MEH-PPV filled microcavity tuned to 580 nm



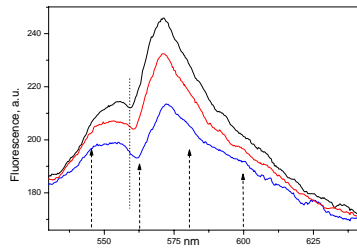
Red: Emission spectrum on a microcavity (half width at half max ~ 12 nm)

Black: Reflectance spectrum

Top layer has large pores

The pore structure and layering can be used to control the shape of the emission spectrum

Exposure to TNT



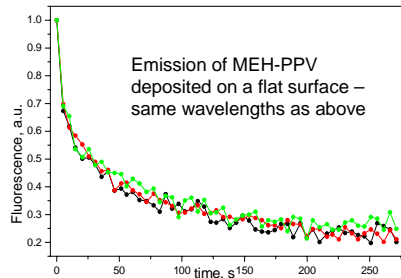
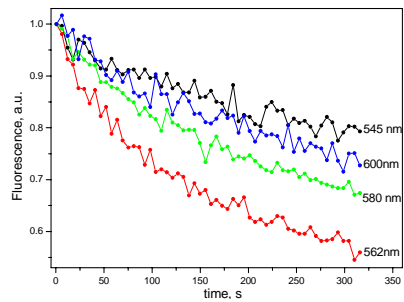
Black: Emission from unexposed sensor

Red: Emission after 50 sec exposure to TNT

Blue: Emission after 250 sec exposure to TNT

Arrows indicate wavelengths used for the time dependence of the emission decay shown in the upper right figure.

Note the shift of the spectral "hole" as a function of TNT exposure – this provides one additional response for a multiplexed sensor

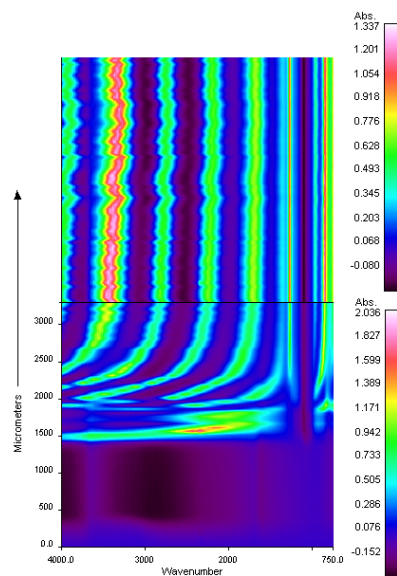


Emission of MEH-PPV deposited on a flat surface – same wavelengths as above

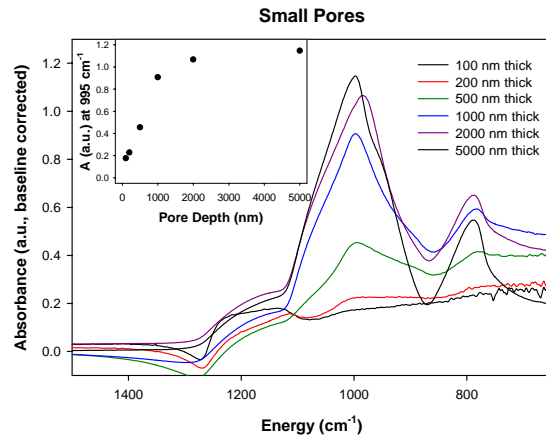
Characterization and Optimization

- Can we measure the uniformity of the pores across the surface?
- Can we measure the pore depths, nondestructively?
- How do we optimize the use of the pores – do we know when the pores are filled?
- How do we determine how much of the pore structure is filled, nondestructively?

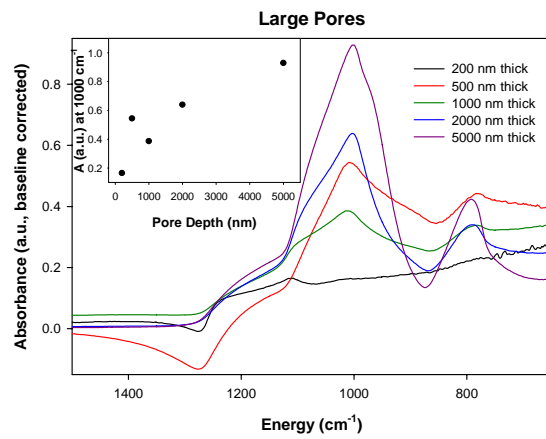
Pore Distribution – without an SEM



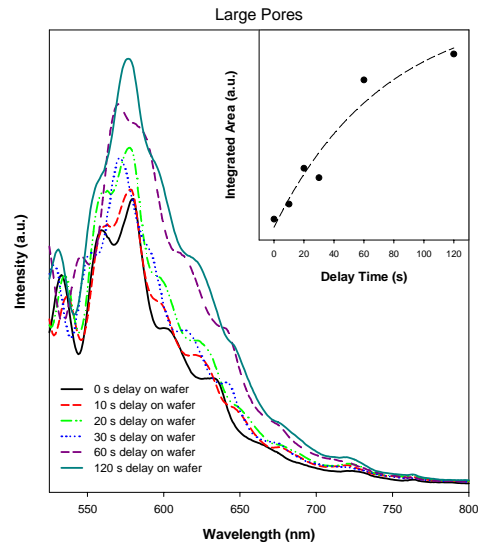
Pore Depth – ATR-FTIR of SiO₂



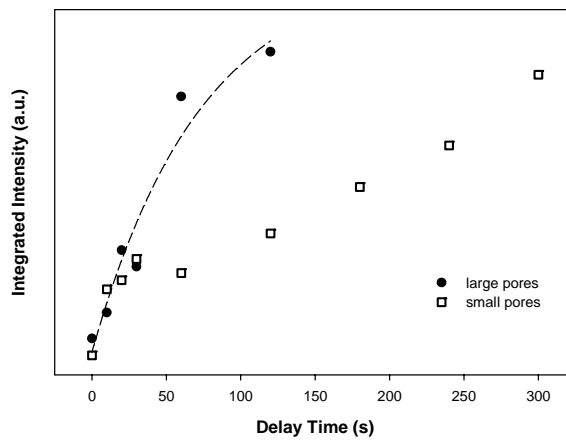
Pore Depth – ATR-FTIR of SiO₂



Pore Filling – Effectiveness of Spin-Casting

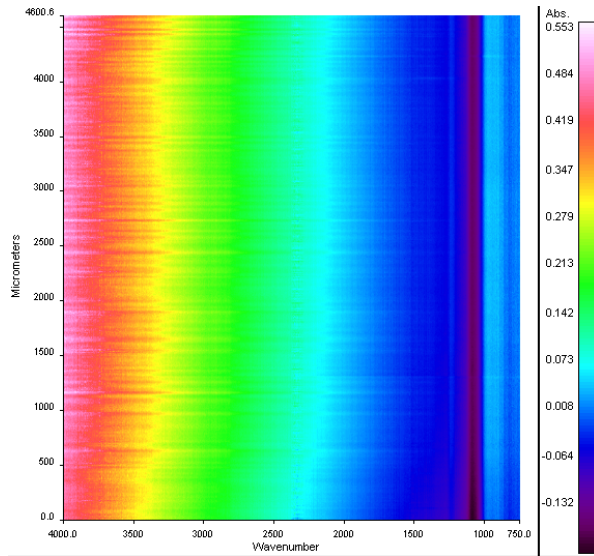


Pore Filling – Effectiveness of Spin-Casting



- Both large and small pores can be filled with equivalent amounts of polymer
- After ~40 sec on the wafer the mechanism of pore filling changes

Polymer Distribution



The polymer distribution is even over the spin-cast area. The fine structure is attributed to the un-etched areas of the sample.

Conclusions

- Porous Silicon provides additional transduction mechanism for sensory applications
- Pore thickness can be monitored by IR spectroscopy of the SiO_2 layer
- Filling of pores by the polymer can be monitored by the fluorescence
- Spin-casting conditions can be used to control pore filling

Acknowledgments

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