SAND2020-9924C

Chemical Warfare Agent Detection Using Zirconium Metal-Organic Framework Functionalized Plasmonic Sensors

Christian Pattyn[1], Leah N. Appelhans[1]*, Jayson Briscoe[1], Lindsey Hughes[1], Bonnie McKenzie[1], Mark Rodriguez[1], James Griego[1], Matthew Moorman[1], Esther Frederick[1], Erika Vreeland[1], Dale L. Huber[2], Karl Westlake[1], Anthony Chavez[1], Jeremy B. Wright[1]*

*Corresponding authors: lappelh@sandia.gov; jbwrigh@sandia.gov

[1]Sandia National Laboratories, Albuquerque, NM 87123; [2]Center for Integrated Nanotechnologies, Sandia National Laboratories, Albuquerque, NM 87185

U.S. DEPARTMENT OF ENERGY

Office of Science

cint.lanl.gov

Introduction

We are seeking to develop a functionalized extraordinary optical transmission (EOT) plasmonic sensor for the purpose of detecting low-levels of gaseous chemical warfare agents (CWAs).

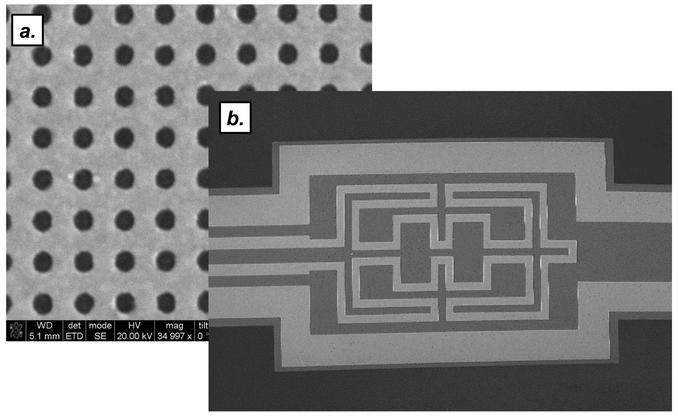


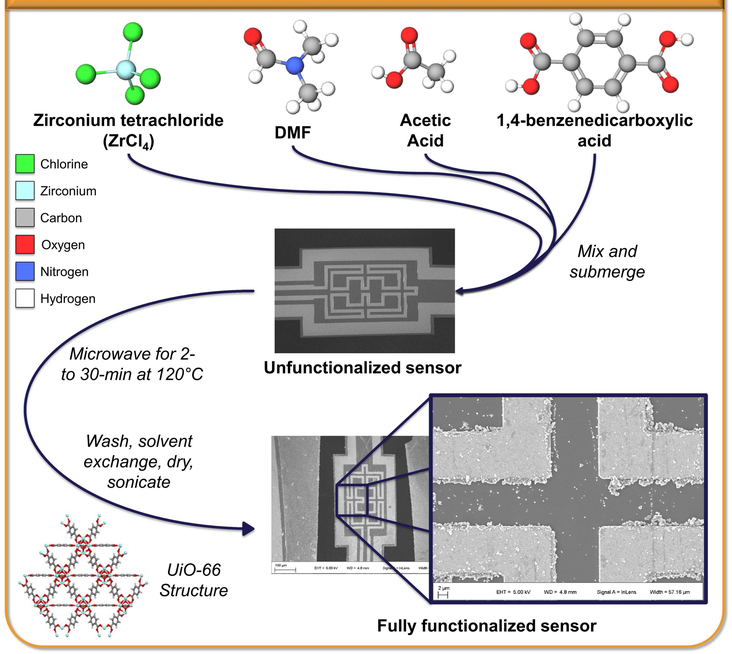
Figure 1. *Unfunctionalized sensor substrates,* ***a)*** *nanohole array (NHA) EOT sensor and* ***b)*** *plasmonic sensor.*

Current work focuses on the development of a zirconium based metal-organic framework (MOF) film coating to functionalize silicon and gold sensor substrates.

This MOF is currently being tested on NHA glass substrates for detection of the CWA simulant, DMMP.

This poster details a facile microwave synthesis method and sensor functionalization with UiO-66 thin films, and initial tests with DMMP.

Synthesis



Results: Sensor Functionalization

With further optimization for thin film growth for temperature, time, and initial reagent concentrations, we found that homogeneous, oriented thin films of UiO-66 and UiO-66-NH_2 could be grown on gold with reaction times as short as 2 minutes.

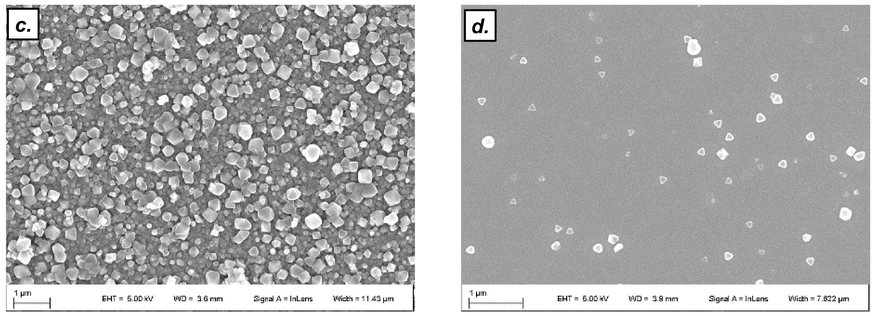


Figure 2. *SEM imaging of blank substrates coated with UiO-66 MOF,* ***c)*** *silicon substrate and* ***d)*** *gold substrate.*

The films consist of relatively large intergrown crystallites with a dense, thin base of small domains. The films consistently showed variation in thickness on silicon substrates. Films grown on gold substrates showed no consistent variation across synthesis conditions. Though they did show some variation experiment-to-experiment individual films were highly homogenous.

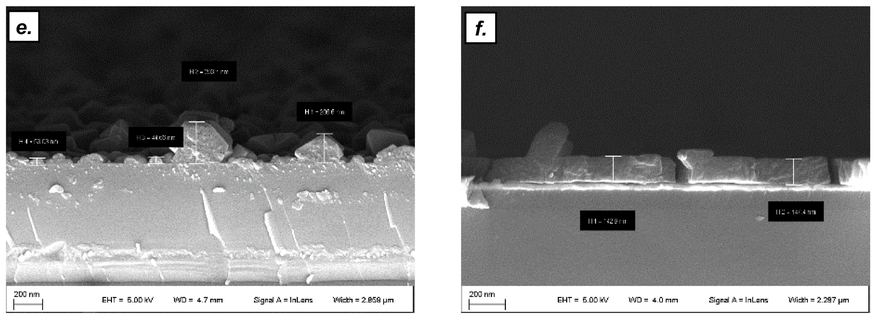
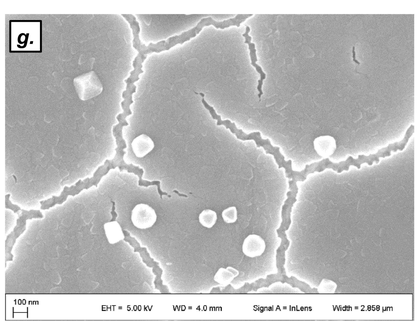


Figure 3. *SEM imaging of blank substrates coated with UiO-66 MOF,* ***e)*** *silicon substrate and* ***f)*** *gold substrate.*

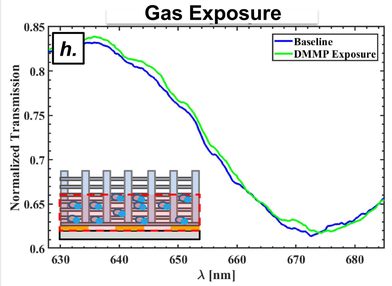
Multiple reaction times were investigated over the course of the experiment, and films were grown following 2, 5, 15, 30, and 60 minute reaction times at 120°C. Though longer reaction times (30 and 60 min) exhibited slightly more overgrowth the effect was not dramatic. In fact, film thickness was not strongly correlated to reaction time, as there was similar sample-to-sample variation for the base conditions (30 min, 120 °C) as there was for samples synthesized with differing reaction times.

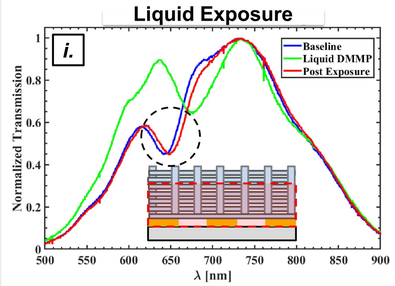
In contrast to other thin film growth methods for UiO-66, some of the films synthesized on gold substrates by the microwave method presented a surface fracturing of unknown origin (**Fig g**). It is thought that this fracturing could be helpful or harmful to the deployment of these sensors, depending on the overall presented chemical selectivity.



Results: Initial Sensor Performance

UiO-66 functionalized NHA sensors on glass were exposed to gaseous DMMP, a CWA simulant. The exposure created a measurable spectral shift in the sensor, as can be seen in **Fig. h**. This spectral shift is caused by a number of DMMP molecules being trapped in the UiO-66 matrix, which increases the index seen by the plasmonic field.





The sensors were also exposed to liquid DMMP, as shown in **Fig. i**. which instead caused a collapse of the UiO-66 matrix. This collapse caused a permanent post-exposure spectral shift. This collapse effectively caused a permanent index by the plasmonic field.

The above changes in the refractive index adjust the overall optically transmitted spectrum, which allow our direct analysis of surface behavior within the plasmonic field on the sensor.

Conclusions & Future Work

We report a simple, rapid microwave synthesis method for the growth of thin films of UiO-66 for use in chemoselective functionalization of gold and silicon sensor substrates. This method can provide high-quality thin films in as little as 2 minutes.

Future work will include the testing of the microwave synthesis for different types of MOFs. We will also utilize a gas flow cell in conjunction with a quartz crystal microbalance (QCM) sensor to analyze simulant uptake of the UiO-66 and other MOF thin films while exposed to a variety of CWA simulants mixed with other chemicals, to test sensitivity and selectivity of the MOF.

Figure 4. *Future work* ***j)*** *standard QCM sensor and* ***k)*** *gas flow cell.*

SAND NUMBER

This work was primarily supported by the Defense Threat Reduction Agency (Grant No. HDTRA-1929358). This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. DOE's National Nuclear Security Administration under contract DE-NA-0003525. The views expressed in the article do not necessarily represent the views of the U.S. DOE or the United States Government.