

# Metal Organic Framework-Coated Optical VOC Gas Sensor

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**Abstract**—We report a metal organic framework (MOF)-coated nanohole array based plasmonic gas sensor. Arrays of 200 nm circular holes are fabricated with a period of 400 nm. About 10 nm thick MOF is coated on the sensor platform to provide high sensitivity and near real-time response to gases.

## I. INTRODUCTION

Plasmonic sensors have been applied for years [1]–[4]. Many people use them as biosensors because they can provide high sensitivity and selectivity with specific functional coatings [3], [4]. Few applications of plasmonic gas sensors were reported in recent years due to the small sensing signal, especially when sensing gases with low concentrations (nmol/mol to sub  $\mu\text{mol/mol}$ ) [5]–[7]. Metal organic frameworks (MOF) as gas sensing materials have been studied for years [8], [9]. However, only Van Duyne’s group reported a MOF-coated plasmonic gas sensor [8], [10]. Sensing of gases at low concentrations, for example, volatile organic compounds (VOCs), with MOF-coated plasmonic gas sensors has not been reported yet. The demand for sensing trace VOCs has been increasing recently, especially in the human health area. Studies show that VOC gases in exhaled human breath can be used as biomarkers to predict and study potential diseases in early stages, such as lung cancer and diabetes [11], [12]. In this work, we report a MOF-coated nanohole array sensor (NHA) that could be used to detect VOCs like acetone and ethanol (major VOC gases in human breath) at 5  $\mu\text{mol/mol}$  (ppm). The design and prototype fabrication were reported in previous work [13]. In Section II, we will discuss multi-device fabrication process and methods to coat the sensors with Cu-1,3,5-benzenetricarboxylic acid (Cu-BTC) MOF using a layer-by-layer process. In Section III, we will discuss the results of testing the sensor under exposures to 5  $\mu\text{mol/mol}$  (ppm) of acetone and ethanol.

## II. METHODS

Design and fabrication aspects for the bare NHA sensor prototype were reported previously [13]. In this work, we applied a different approach, which is suitable for fabricating large numbers of samples. Figure 1 shows the fabrication

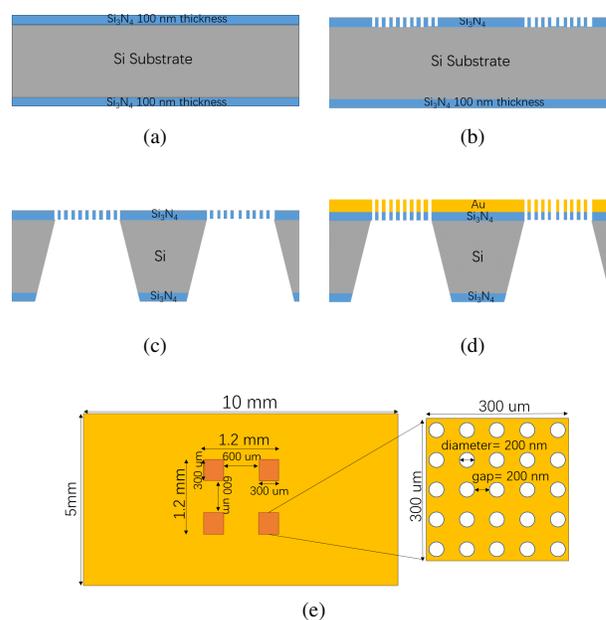


Fig. 1: Fabrication process for the NHA sensor. (a) Coat 100 nm thick  $\text{Si}_3\text{N}_4$  on a Si substrate with LPCVD. (b) Pattern 200 nm circular hole array with deep UV stepper and RIE etching. (c) Pattern the membrane window on the backside  $\text{Si}_3\text{N}_4$  layer with mask aligner and RIE etching. Then etch Si to create the membrane by KOH etching. (d) Deposit 5 nm Ti + 80 nm Au on top of the sample with E-beam evaporator. (e) Top view of the chip. The sensor cells show red color due to the specific sized NHA pattern.

process schematically. Over 100 4-sensor chips could be made each time on a 100 mm wafer. Each 4-sensor chip was first submerged in a self-assembling-monolayer (SAM) solution (100  $\mu\text{mol/L}$  4-mercaptobenzoic acid ethanolic solution) for 1 hour. Then we adapted the method from reference [14] to coat 10 layers of MOF on the sample. To avoid breaking the

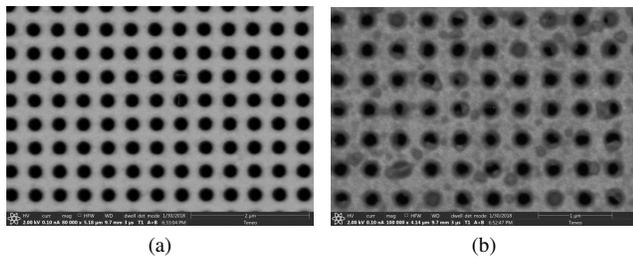


Fig. 2: SEM image of the sample (a) before, and (b) after MOF coating

suspended platforms, we used a shaker instead of a sonicator during the coating process.

The 4-device sample was characterized by a scanning electron microscopy (SEM) after coating with MOF. Figure 2 shows the SEM image of a region of a NHA sensor before (a) and after (b) coating with the MOF. The diameter of the holes shrank  $\approx 20$  nm after coating, which suggests the thickness of the MOF was  $\approx 10$  nm ( $\approx 1$  nm/layer).

### III. RESULTS

After characterizing the sensor, we tested one of the four on-chip sensors under 5  $\mu\text{mol/mol}$  (ppm) of acetone and ethanol, sequentially. Each gas was tested for 4 sequential cycles to examine experimental reproducibility. A reflection-based setup was used in the testing [13]. The testing results are plotted in Figure 3. The blue line shows the result for acetone and the red line shows the result for ethanol. Even though these two gases are similar in chemical structure, the sensor shows differences in the responses. For the same concentration, acetone has a signal 50 % larger than the one of ethanol. However ethanol is absorbed and released faster by the MOF coating. The biggest advantage of the sensor is that it can provide near real-time sensing. The sensor's response saturates in less than 1 min, and recovers in less than 2 min. With the help of this technology, one can easily study the transition stage of the gas sensing process. Faster sensing speeds provide information such as rise times and recovery times. This information can be used to analyze the target gases in multiple dimensions, and help to separate gases.

### IV. CONCLUSION

In this paper, we reported a Cu-BTC MOF-coated NHA plasmonic gas sensor. With the help of the coated MOF layer, the sensor can detect gases at low concentrations with fast responses. The technology can also be used for gas separation/discrimination by analyzing the rise time, saturation signal and release time together.

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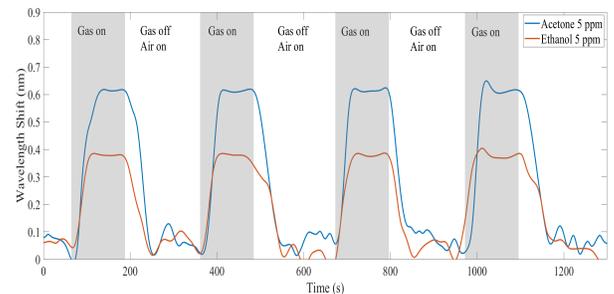


Fig. 3: Measurement result of the NHA sensor exposed under 5  $\mu\text{mol/mol}$  (ppm) of acetone and ethanol. Each testing cycles is 5 min with 2 min gas exposure and purging by 3 min dry air flush. The blue line shows the result of acetone and the red line shows the result of ethanol.

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