SCALABLE ULTRA LOW-POWER CHEMICAL SENSING WITH METAL-ORGANIC FRAMEWORKS

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ABSTRACT

This paper reports the innovative use of a highly tunable material, metal-organic frameworks (MOFs), for chemical sensing on an ultra-low-power platform based on a field-effect transistor. We demonstrate proof-of-principle devices functionalized with two MOFs: "HKUST-1" for humidity sensing and "ZIF-8" for reversible NO_2 detection. These devices show minimal drift, yield highly reproducible responses, recover rapidly, and have excellent selectivity. Through this approach, devices with minimal power draw and high selectivity could be widely distributed for continuous environmental and safety monitoring.

KEYWORDS

Gas sensing, field-effect transistor, metal-organic frameworks, self-assembled monolayers.

INTRODUCTION

Developing technologies for distributed chemical sensing as part of the "Internet of Things" will rely on ultra-low power sensors with high selectivity, sensitivity and stability. One such device, the chemically sensitive field-effect transistor (CS-FET) (Figure 1), has a power draw of <10 microW, form factor of 1 cm x 1 cm, and has been demonstrated with NiPd nanoparticles for sensitive H_2 detection with high fidelity [1]. The CS-FET is structurally similar to a standard field-effect transistor, except the gate metal is replaced by a sensing layer whose work function shifts when gas molecules adsorb to the surface. The most common sensing materials are metals, which are easily deposited through standard microfabrication techniques. However, metal nanoparticles lack the tunability required for targeted, selective chemical sensing. Therefore, the development of sensing materials with greater sensitivity is needed to improve the performance of the CS-FET devices.

Another problem that limits the utility of the CS-FET is the strong tendency for water to adsorb at the exposed hydrophilic Si-OH terminations at the dielectric SiO_2 surface. SiO_2 can be passivated with hydrophobic self-assembled monolayers such as octadecyltrichlorosilane (OTS). The impacts of an OTS layer on the SiO_2 for sensing responses are unclear, and we estimate that such a monolayer could decrease the capacitance of the dielectric – and therefore the sensing response – by half [2].

One intriguing class of materials for chemical sensing is metal-organic frameworks. MOFs are porous, crystalline structures comprising metal nodes and organic linkers. Two examples that are studied in this manuscript are shown in Figure 2. The properties of the MOFs can be tuned by judicious choice of metal and linker towards selective adsorption. For example, the MOF "HKUST-1" is hydrophilic, and is well suited to absorb humidity [3], whereas the MOF "ZIF-8" tends to absorb acidic gasses quite easily because of its zinc sites [4]. MOFs are an exciting class of materials for chemical sensing on the CS-FET because the chemical adsorption events that trigger work function changes in the MOF membrane are highly MOF – analyte specific [5] and because many MOFs can be grown as thin films through solvothermal conditions on a variety of surfaces [6].

In this paper, we demonstrate how two MOFs – HKUST-1 and ZIF-8 – can be integrated with the CS-FET for selective chemical sensing of humidity and NO_2 without using a microheater.

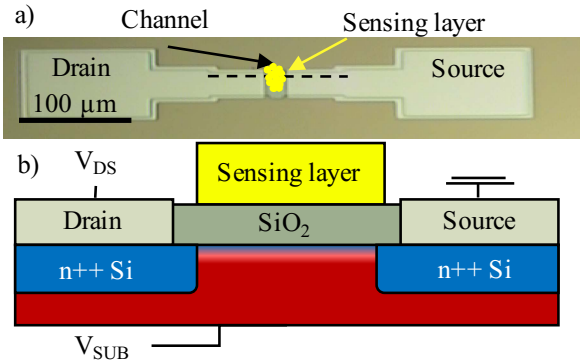

Figure 1: (a) optical image of the device with a sensing layer sketched over the channel. (b) Cartoon cross-section of the device indicating the drain-source and substrate bias V_{DS} and V_{SUB}, respectively.

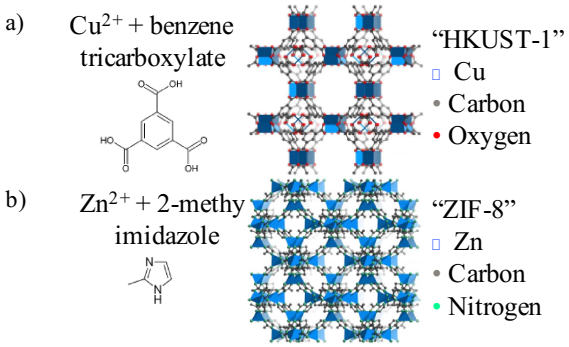

Figure 2: Metal-organic frameworks are made up of metal nodes connected by linkers. Shown are the structures of (a) HKUST-1 and (b) ZIF-8.

EXPERIMENTAL

Device Preparation

Devices are fabricated using a standard method on bulk silicon wafers [1]. The source/drain contacts are W on Ni and the effective oxide thickness of the SiO_2 between the sensing layer and the bulk silicon is approximately 5 nm.

In all tests, a chiplet of <100> silicon followed the device to characterize the resulting film. All surfaces were cleaned in acetone, isopropyl alcohol (IPA), water, and with a 10-minute exposure to UV light and ozone to prepare a pristine surface.

The MOF HKUST-1 was prepared with a layer-by-layer method, where one layer of MOF was added sequentially [6]. The devices were submerged in an ethanolic 50 mM solution of copper acetate, rinsed in fresh ethanol, submerged in an ethanolic 100 mM solution of benzene tricarboxylic acid, and rinsed again in ethanol. These four steps completed one cycle, which took about 1 minute. A total of 60 cycles was used for all HKUST-1 devices discussed in this work. This method allowed us to grow a layer of HKUST-1 at the surface of the device. Solvothermal methods for this MOF produced irregular growth that did not always cover the channel. The synthesized HKUST-1 was activated and stored in vacuum.

Octadecyltrichlorosilane (OTS) self-assembled monolayer deposition was done by a standard method [7]. 100 microliters of OTS was dissolved in 100 mL toluene at room temperature. The cleaned devices were exposed to 50% relative humidity air for one hour before submerging in the toluene and OTS bath. The devices were left in the bath for one hour, then rinsed with toluene, stored in a bath of toluene for 24 hours, dried in nitrogen, and stored for later use.

The MOF ZIF-8 was deposited in a solvothermal manner. The device was submerged in a methanol solution containing 20 mM zinc nitrate and 100 mM 2-methylimidazole for 30 minutes at room temperature. The device was then submerged three more times in baths of the same composition for the same time for a total of four baths and two total hours [8]. The synthesized ZIF-8 was activated in a bath of dimethylformamide overnight and stored in vacuum.

Characterization

X-ray diffraction (XRD) spectra were taken using a Bruker AXS D8 Discover GADDS XRD diffractometer system with a grazing angle of 0.3° and a Cu Kα source. Scanning electron microscopy was done one a Phenom Pro benchtop SEM at 15 kV beam energy.

Gas Sensing

All gas sensing measurements were carried out in a walk-in fume hood. Devices were wire bonded to a 28-pin J-bend leaded chip carrier. A small-volume (~ 0.83 cm^3) 3D printed housing, made of polylactic acid, consisting of a ¼-inch gas inlet was used to cover the chip carrier. Synthetic dry air was used as diluent gas and was procured from Praxair Technology Inc. Synthetic air–diluted gas cylinders were purchased from MESA International Technologies Inc. at a calibrated concentration. Typical gas flow rates were from 1 to 100 sccm, and diluent (synthetic air) flow rate was 100-1000 sccm. Humidity was controlled by diverting the diluent through a bubbler filled with 18 MΩ-cm deionized water. Ambient temperature and humidity were monitored by commercial sensors purchased from Sensirion AG (models SHT2x and SHT3x). Gas delivery was controlled by mass flow controllers (Alicat Scientific Inc.). CS-FET sensors were biased using a Keithley 428 current preamplifier, and the current signals were acquired using a LabVIEW-controlled data acquisition unit (National Instruments, NI USB-6259). Unless otherwise mentioned, the sensing measurements in this manuscript were recorded with source-drain voltage, V_{DS} = 3 V, and substrate bias, V_{SUB} = 0 V. The current measured was unambiguously determined to be through the channel by measuring the resistance between two points on the silicon wafer that was coated in MOF, finding that the MOF thin films were unable to carry current.

RESULTS AND DISCUSSION

Synthesis results

The structures of the MOFs are confirmed through XRD (Figure 3) where our films show diffraction patterns which are in good agreement with the calculated structures. Both HKUST-1 spectra show broadness in the main peak, indicating small domain sizes, which is consistent with films deposited in the layer-by-layer method at room temperature [6]. The ZIF-8 spectrum shows a preferred orientation compared to the simulated powder, in good agreement with other room-temperature syntheses of ZIF-8 crystals [8].

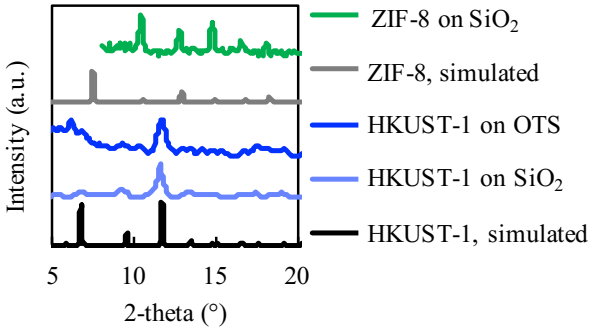

Figure 3: XRD of prepared samples and simulated XRD spectra for HKUST-1 [3] *and ZIF-8* [8].

The MOF thin films have nearly conformal coating over the channel, as shown by optical images of the device and SEM images of the channel (Figure 4). The HKUST-1 SEM image (Figure 4e) shows aggregates forming over the HKUST-1 thin film that are typical in our synthesis method [6]. No difference was observed for the HKUST-1 sample on OTS. The ZIF-8 sensing layer nearly coats the channel with ~500 nm particles.

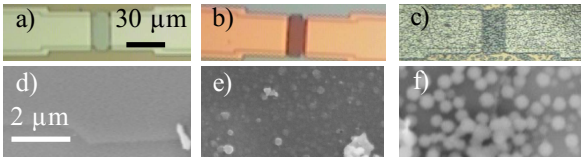

Figure 4: Optical images of devices. (a) bare, (b) HKUST-1, (c) ZIF-8. SEM images of device channel of (d) bare, (e) HKUST-1, and (f) ZIF-8.

HKUST-1 Chemical Sensing

HKUST-1 is one of the most hydrophilic MOFs [3], so we predicted that it should be a highly responsive chemical sensor for humidity. However, we first found that the device with just HKUST-1 did not respond quickly nor recover at a reasonable time scale (Figure 5a). We hypothesized that the hydrophilic Si-OH at the silicon dioxide surface was convoluting the HKUST-1 response.

To improve the performance of the HKUST-1 humidity sensor, we coated the SiO_2 with a hydrophobic OTS monolayer. Water contact angle measurement of the OTS film on a silicon wafer that followed the device through the OTS synthesis showed a contact angle of 110º, indicating exceptional quality of the OTS film [7]. To verify that we had prevented humidity adsorption, we tested the OTS device to humidity, finding essentially no response to humidity (Figure 5b). The HKUST-1 on OTS device responds to humidity with a normalized response of 15x at 0 V_{SUB} and nearly 200x (i.e., 20,000% of initial current) at -2 V_{SUB} for the humidity range 5-16% (Figure 5c) and recovers within seconds. These tests show that a dielectric based on SiO_2 and OTS does not inhibit the sensing performance of an HKUST-1 film for humidity sensing. We may observe greater response because of the orientation of the HKUST-1 crystals on the OTS compared to silicon [6], but more work is needed to determine the effect of crystal orientation on work function response.

HKUST-1 is a selective sensing material, showing no response to H_2, CH_4, H_2S, SO_2, CO_2, or NO_2 (Figure 6).

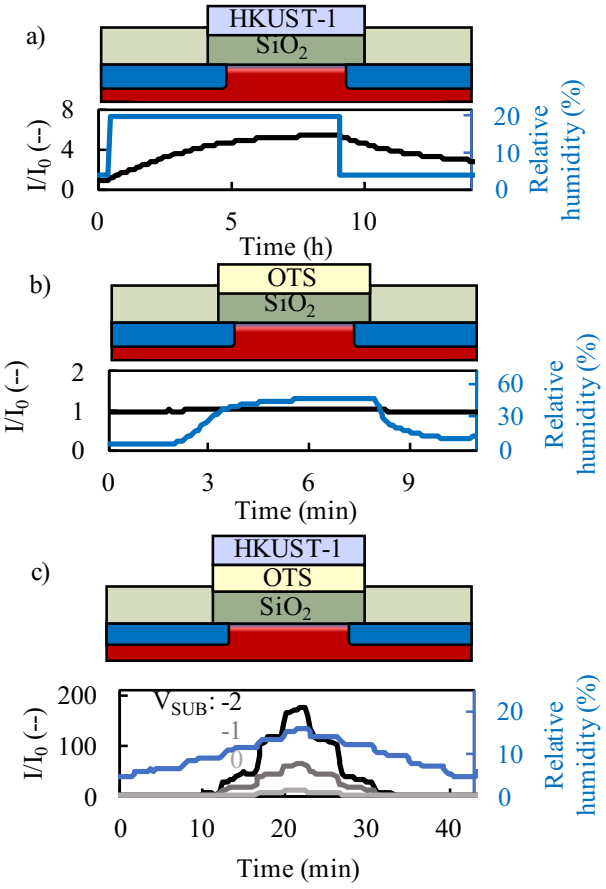

Figure 5: Humidity response of sensor with (a) HKUST-1 on SiO_2, (b) OTS on SiO_2, (c) HKUST-1 on OTS on SiO_2.

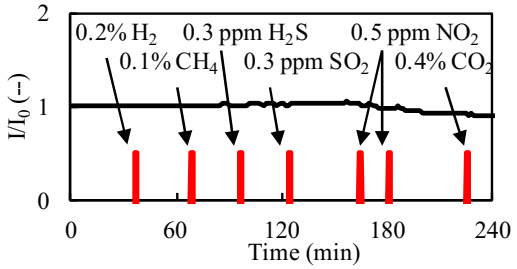

Figure 6: Selectivity tests for HKUST-1 on OTS.

ZIF-8 Chemical Sensing

Following these promising results, we moved to another well-characterized MOF, ZIF-8. ZIF-8 can adsorb acidic molecules at zinc sites throughout the structure [4], which makes it a good candidate for sensing NO_2. The adsorption and desorption are mediated by mild humidity (~ 20%) [4] and so, we targeted our sensing experiments in these atmospheric conditions. The sensing result is given in Figure 7 for V_{SUB} ranging from 0 to -2 V. The framework responds repeatably to NO_2 and the sensor current returns to the initial value without use of a microheater, indirectly suggesting that the framework can recover from the NO_2 adsoprtion. We used an on-stream humidity sensor to ensure that the humidity did not change during the exposure. More work, such as in-situ spectroscopy, is needed to understand if the material truly recovers or if the recovery in current is due to a separate mechanism. Assuming a 3-standard deviation about the baseline current for -2 V_{SUB}, we calculate that the limit of detection is 20 ppb NO_2.

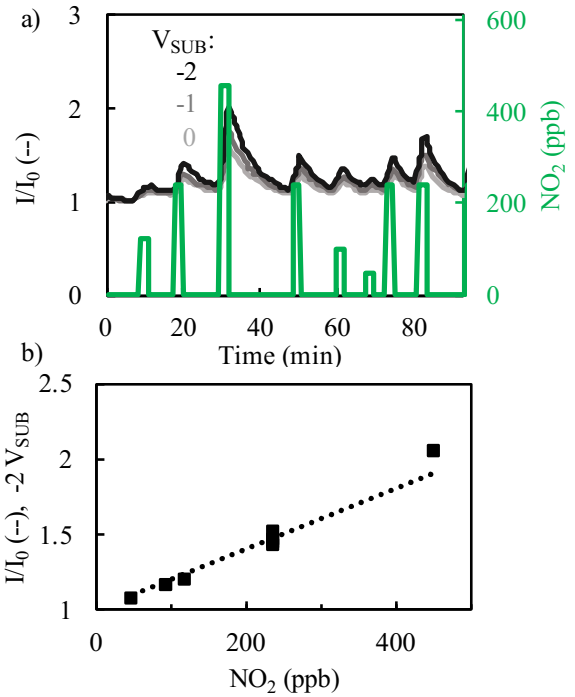

Figure 7: (a) NO_2 sensing response in 20% relative humidity air for ZIF-8. (b) sensitivity plot at -2 V_{SUB}. The dashed line is a guide to the eye.

Like HKUST-1, ZIF-8 is a very selective sensing material, with no response to H_2, CH_4, CO_2, SO_2, or H_2S in 20% relative humidity air. (Figure 8).

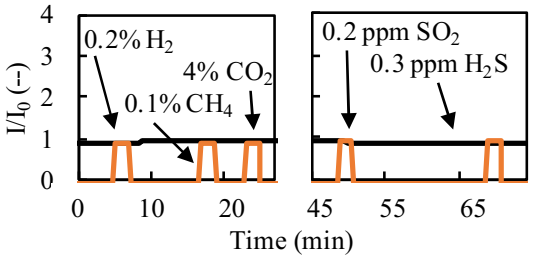

Figure 8: Selectivity tests for ZIF-8 in 20% relative humidity air.

The sensing experiments in this manuscript are clearly differentiated from the response of the bare, unfunctionalized sensor, shown in Figure 9.

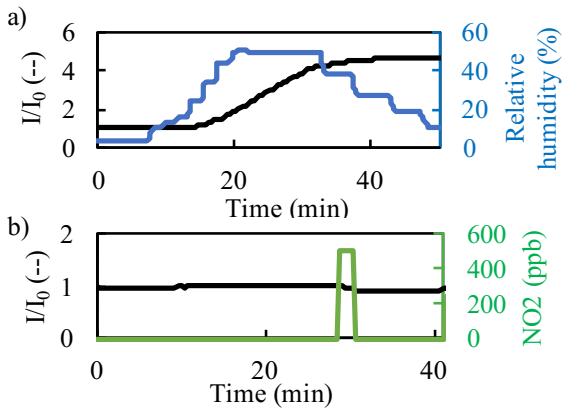

Figure 9: Bare sensor responses to (a) humidity and (b) NO_2 in 20% relative humidity air.

CONCLUSIONS

Two MOF thin films were used for selective chemical sensing on the CS-FET platform. The advantage of the CS-FET platform is the low power draw (<10 uW) and low form factor. In the first sensing film, we were inspired by the high affinity that HKUST-1 has for water vapor to use it as a humidity sensor. Although the silicon dioxide dielectric initially convoluted the response, we were able to reduce the impact of the silicon dioxide by passivating it with a hydrophobic monolayer, octadecyltrichlorosilane. The device has a robust response and responds and recovers within seconds. HKUST-1 has no cross-sensitivity to hydrogen, methane, hydrogen sulfide, sulfur dioxide, or nitrogen dioxide. The second film we prepared was ZIF-8 for NO_2 sensing. ZIF-8 has defect sites that bind strongly to acidic gasses such as NO_2. The device recovers without a microheater to the initial current. ZIF-8 has no sensitivity to hydrogen, methane, hydrogen sulfide, nor sulfur dioxide. These are just two of the thousands of MOFs that could be prepared as sensing films for targeting many other gases.

ACKNOWLEDGEMENTS

We would like to thank the Berkeley Sensor and Actuator Center (BSAC) and the National Science Foundation (NSF) for their support of this project. Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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