

Organic Field Effect Transistor Fabrication

CNF Project Number: 863-00

Principal Investigator(s): John A. Marohn

User(s): Peter Sun, Rachael Cohn

Affiliation(s): Department of Chemistry and Chemical Biology, Cornell University

Primary Source(s) of Research Funding: National Science Foundation

Contact: jam99@cornell.edu, hs859@cornell.edu, rc784@cornell.edu

Website: <http://marohn.chem.cornell.edu/>

Primary CNF Tools Used: Autostep i-line Stepper, Oxford 80+ Etcher, Oxford ALD FlexAL

Abstract:

We fabricated field-effect transistors with an integrated source-drain electrode silicon wafer with an improved liftoff process and an extra layer of hafnium dioxide (HfO_2).

Summary of Research:

Lead halide perovskites are an emerging class of semiconductors that have shown promising optoelectronic properties. The ability of lead-halide perovskites to maintain exemplary photovoltaic properties while being riddled with structural defects, mobile vacancies, and mobile ions make lead-halide perovskites unique and worth understanding in microscopic detail. Field-effect transistors (FETs) measurements combined with local Kelvin probe force microscopy is a powerful tool to microscopically study charge motion and charge injection in solution-processed semiconductors.

The transistor substrates consist of gate pads and source-drain pads with interdigitated gold electrodes (5 nm Cr and 30 nm Au) with 5 μm spacing in between. The fabrication was previously developed [1] with a two-step exposure process on Autostep i-line stepper — the gate exposure layer (resist SPR 955 CM 2.1), and the source-drain exposure layer (resist nLOF 2020). The gate pads are etched using the Oxford 80+ etcher, and the gold electrodes are deposited with the odd-hour evaporator. The wafer undergoes a liftoff process and is diced on the DISCO dicing saw.

We have discovered several disadvantages of the previous protocol and improved the fabrication process.

We dramatically increase the yield of the transistors by employing a two-step liftoff process. After being submerged in Microposit Remover 1165 for 12 hours, the wafer is sonicated for six minutes with the solution, followed by a round of IPA spray and water blast cleaning. In the second step, the wafer was sonicated in methanol for three minutes to remove smaller metal particles, subsequently cleaned with IPA and water, and

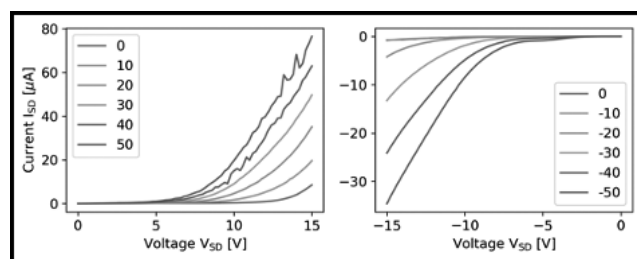


Figure 1: I-V curve for FET made from lead halide perovskite (FAMACs) on substrates fabricated at the CNF. Source-to-drain current (I_{SD}) versus source-to-drain voltage (V_{SD}) at different source-to-gate voltages (V_G). Gate voltage sweep direction: 0 V to 50 V and 0 to -50 V.

dried with N_2 and on hot plate at 110°C for 60 seconds. The yield improved from 57% to 95%, determined by if the source-drain is shorted due to metal remains on the electrodes.

However, bottom-gate bottom-contact perovskite FETs are difficult to successfully solution process and operate, presumably due to gate voltage induced ion motion and gate material induced material degradation from the widely used gate oxide SiO_2 [2].

Here, we modified and improved our existing FET substrate fabrication recipe to replace the SiO_2 gate with high-K material hafnium oxide, HfO_2 , by atomic layer deposition (Oxford ALD FlexAL, 300°C, plasma, HfO_2 , 200 cycles). The exposure time and focus are optimized.

We are still in the process of determining the improvement of the HfO_2 layer over the silicon oxide.

Triple cation lead halide perovskite (FAMACs) was solution-processed onto the resulting transistor substrates in a single step process in a glove box using published methods. The resulting films were annealed at 100°C for one hour. Transport properties were measured in the dark and under the vacuum of 5×10^{-6} mbar. The films showed a noticeable gate effect, which diminished under illumination and repeated measurements (Figure 1). More work is needed to improve the stability of the FETs and understand the effect of gate material and processing on the device performance.

References:

- [1] Hoepker, N. C. "Fluctuations Near Thin Films of Polymers, Organic Photovoltaics, and Organic Semiconductors Probed by Electric Force Microscopy", 2013, Ph.D. thesis, Cornell University, Ithaca.
- [2] Canicoba, N., et al. "Halide Perovskite High-K Field Effect Transistors with Dynamically Reconfigurable Ambipolarity", ACS Materials Lett., 2019, 1, 633-640.

Substrate Preparation for Ultrafast Vibrational Spectroscopy Experiments

CNF Project Number: 1936-10

Principal Investigator(s): Poul B. Petersen

User(s): Stephanie Sanders

Affiliation(s): Chemistry and Chemical Biology, Cornell University; Physical Chemistry II, Ruhr-University Bochum, Germany

Primary Source(s) of Research Funding: National Science Foundation

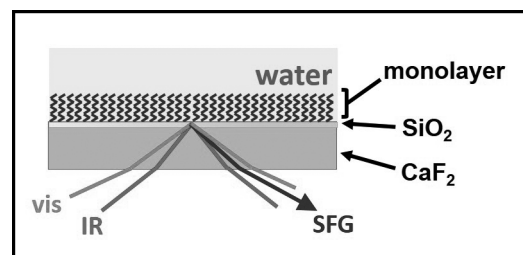
Contact: poul.petersen@rub.de, ses422@cornell.edu

Website: <https://www.ruhr-uni-bochum.de/pc2/petersen/>

Primary CNF Tools Used: Oxford ALD FlexAL

Abstract:

Water is ubiquitous and an active component in many natural and technological processes. Vibrational spectroscopy can be used to probe the structure and dynamics of water in a variety of environments. We use sum-frequency generation, a surface specific vibrational spectroscopy, to probe the structure and dynamics of interfacial water at chemically tunable surfaces. Interfaces with tunable surface character are created with self-assembled monolayers. In order to create substrates compatible for both silane self-assembly and sum-frequency generation, infrared and visible transparent CaF_2 windows are coated with SiO_2 . Then after surface functionalization with silane monolayers, the water structure and dynamics at the interfaces can be explored with sum-frequency generation.



Summary of Research:

Water is an active component in many natural and technological processes [1]. Interfaces terminate the H-bonded network of water. We aim to study the structure and dynamics of water at self-assembled monolayers (SAMs) with varying surface character using sum-frequency generation (SFG) spectroscopy. In SFG, an infrared photon interacts with a dipole transition of the molecule and a visible photon excites the molecule to a virtual electronic state where it can undergo an anti-Stokes Raman transition resulting in a photon at the sum of the two incident frequencies being emitted [2,3].

In order to collect SFG spectra of solid-aqueous interfaces, we must probe through the window so the infrared photons are not absorbed by water. However, silica, a common SAMs substrate, also absorbs in the infrared. To create an infrared and visible transparent substrate compatible with SAMs syntheses, we start with a calcium fluoride (CaF_2) window, which is transparent through the visible and infrared. Then approximately 10 nm of SiO_2 is deposited on the CaF_2 window via atomic layer deposition (ALD) with the Oxford ALD FlexAL. The SiO_2 layer is thin enough to not absorb all the IR photons and prevent SFG spectra of the sample from being collected, but thick enough to form a surface compatible with the self-assembly of silanes.

Once the SiO_2 is deposited, hydrophobic, hydrophilic, or mixed monolayer are synthesized with self-assembly of silanes on the surface. Figure 1 shows a schematic of the surface in contact with water. Then, the surfaces and water at the surfaces are analyzed with SFG [2-6].

References:

- [1] Ball, P. *Life's Matrix: A Biography of Water*; University of California Press: Berkeley, 2001.
- [2] Barrett, A. R.; Petersen, P. B. Order of Dry and Wet Mixed-Length Self-Assembled Monolayers. *J. Phys. Chem. C* 2015, 119 (42), 23943-23950.
- [3] Vanselow, H.; Petersen, P. B. Extending the Capabilities of Heterodyne-Detected Sum-Frequency Generation Spectroscopy: Probing Any Interface in Any Polarization Combination. *J. Phys. Chem. C* 2016, 120 (15), 8175-8184.
- [4] Sanders, S.; Vanselow, H.; Petersen, P. *Water at Surfaces with Tunable Surface Chemistries*. *J. Phys. Condens. Matter* 2018.
- [5] Kocsis, I.; Sorci, M.; Vanselow, H.; Murail, S.; Sanders, S.; Licsandru, E.; Legrand, Y.-M.; van der Lee, A.; Baaden, M.; Petersen, P. B.; Belfort, G.; Barboiu, M. Oriented chiral water wires in artificial transmembrane channels. *Sci. Adv.* 2018 4(3), eaao5603.
- [6] Sanders, S.E.; Petersen, P.B. Heterodyne-Detected Sum Frequency Generation of Water at Surfaces with Varying Hydrophobicity. *J. Chem. Phys.*, 2019, 150 (20), 204708.

Peptoids as Sequence-Controlled EUV-Photoresists

CNF Project Number: 2733-18

Principal Investigator(s): Christopher Kemper Ober

User(s): Florian Hermann Ulrich Kaefer

Affiliation(s): Department of Materials Science and Engineering, Cornell University

Primary Source(s) of Research Funding: JSR Corporation

Contact: cko3@cornell.edu, fhk28@cornell.edu

Website: <https://ober.mse.cornell.edu/>

Primary CNF Tools Used: ABM contact aligner, ASML 300C DUV stepper, AFM Bruker Icon, FilMetrics F50-EXR

Abstract:

Sequence-controlled small molecules were synthesized using a peptide synthesizer. The thus obtained peptoids with an average molar mass of 1000 g/mol and a strong alternating sequence of the two used amines were used as positive tone resists for deep ultraviolet (DUV) and extreme ultraviolet (EUV) lithography. In our first experiments we could demonstrate the potential of peptoids as a promising class of new EUV resist, as both the structure of the used amines and the sequence can be adapted to precisely adjust the properties of the photoresist.

Summary of Research:

Introduction. Today's widely used polymeric resists are typically based on random copolymers. These polymers are polydisperse and relatively large in size, with molar masses ranging from 5,000-15,000 g/mol [1]. Characteristics such as these can have a negative impact on resist performance, and therefore it is necessary to explore other architectures for new resist platforms.

Sequence-Controlled Small Molecules. For sequence-controlled polymers, on the other hand, the monomers are arranged in a specific, user-defined order. Monomer sequence regularity strongly influences the molecular, supramolecular, and macroscopic properties of polymer materials, showing promise for the creation of a new

type of small molecule photoresist. In this respect, peptoids represent a particularly advantageous group, since they can be specifically varied in their structure, length and sequence of the amines used [2].

Peptoid Synthesis. A solid phase peptoid synthesis approach using a 2-chlorotrityl based resin was used [3]. After activating the resin with bromoacetic acid, the first amine solution was added. After the reaction was completed, the second amine, which contains a tert-butyl protecting group, was added and clicked to the resin. These steps were repeated until a peptoid with a total length of ten amines in alternating sequence was obtained, see Figure 1. Subsequently, the peptoid was cleaved from the resin under mild acetic conditions, purified and dried. In order to determine the molar mass and the molecular structure liquid chromatography-mass spectrometry was used.

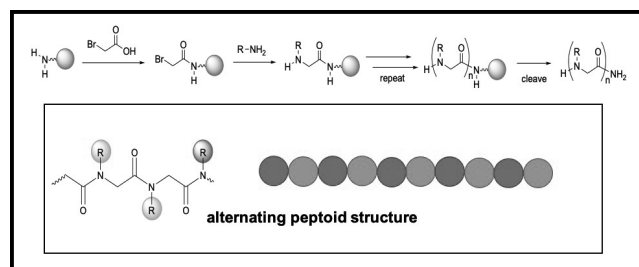


Figure 1: Synthesis of peptoids with an alternating amine sequence.

Characterization and Results:

Preliminary photolithography experiments were performed on the ABM contact aligner and the DUV stepper. For this purpose, the produced peptoid sample with a molar mass of 1000 g/mol and an alternating amine sequence was dissolved, and spin-coated on a silica wafer.

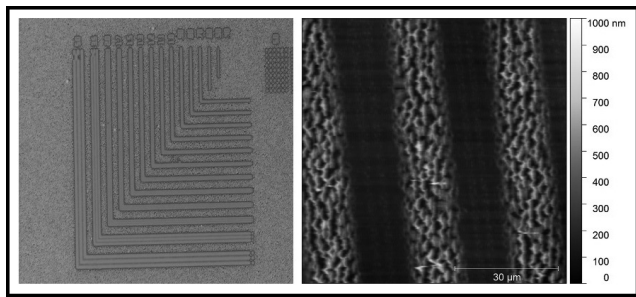


Figure 2: Patterned peptoid film after DUV exposure at the ABM contact aligner. (left) light microscopy image, (right) AFM image.

The resist film thickness was measured by FilMetrics F50-EXR. The made samples were exposed using the ABM contact aligner and developed using a diluted tetramethylammonium hydroxide (TMAH) solution. The obtained pattern was characterized using light microscopy and atomic force microscopy (AFM Bruker Icon), see Figure 2.

The measurements carried out successfully prove that peptoids can be used as DUV photoresist materials. However, the obtained results also show that further optimization of the peptoid structure as well as the photolithographic process requires further optimization. Especially the achieved resolution and the obtained mean roughness of 45 nm have to be improved.

Conclusions and Future Steps:

Sequence controlled peptoids with a molar mass of 1000 g/mol and with strong alternating sequence of the used amines could be synthesized and successfully used as positive tone photoresist using the ABM contact aligner. The obtained patterned films were characterized using light- and atomic force microscopy. However, several challenges still need to be solved. How do we design small molecules to make a photoresist with a desired property? How do we control the nanoscale resolution of the resulting resist? The aforementioned questions shall be studied and answered in the future.

References:

- [1] Patterson, K.; Yamachika, M.; Hung, R.; Brodsky, C.; Yamada, S.; Somervell, M.; Osborn, B.; Hall, D.; Dukovic, G.; Byers, J.; Conley, W.; Willson, C. G., *Polymers for 157-nm photoresist applications: a progress report*. SPIE: 2000; Vol. 3999.
- [2] Gangloff, N.; Ulbricht, J.; Lorson, T.; Schlaad, H.; Luxenhofer, R., *Peptoids and Polypeptoids at the Frontier of Supra- and Macromolecular Engineering*. *Chemical Reviews* 2016, 116 (4), 1753-1802.
- [3] Culf, A. S.; Ouellette, R. J., *Solid-phase synthesis of N-substituted glycine oligomers (alpha-peptoids) and derivatives*. *Molecules* (Basel, Switzerland) 2010, 15 (8), 5282-5335.