

Construction and Electrical Characterization of 0.9 nm Tall Channels Made via Pyryl Phosphonic Acid (PYPA) Self-assembly

Jianchun Dong¹, Babak A. Parviz¹, Hin L. Yip², Hong Ma², and Alex K-Y. Jen²

¹Department of Electrical Engineering, University of Washington, Seattle, WA 98195-2500

²Department of Materials Science and Engineering, University of Washington, Seattle, WA 98195-2120

Abstract

Molecular self-assembly can yield well-defined systems for charge carrier transport for the construction of a variety of devices such as field effect transistors and biosensors. In this paper, we present a simple method to construct a nano conductive channel by exploiting self-assembly of pyryl phosphonic acid (PYPA) molecules. By spincoating an ethanolic solution of PYPA on a silicon dioxide surface, we were able to form a conductive channel between a pair of pre-patterned Cr/Au electrodes. We used X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) to characterize the PYPA self-assembled film. We then measured the current-voltage curves and current-temperature curves of the fabricated devices. By utilizing the specific reaction between the phosphoric acid moiety and silicon dioxide surface, we provide a straightforward method to integrate the nanometer size conduction channel with the complementary metal oxide semiconductor (CMOS) integrated circuits in a one-step post-process procedure.

Introduction

To face the approaching challenge posed by reaching the limit of “Moore’s Law” in microelectronics industry, numerous nano-scale electronic components have been developed and characterized[1-4]. Through a bottom up approach, making nano-scale functional devices through self-assembly has been one of the promising methods to engineer wires[5, 6], field-effect transistors[7], memory cells[8], and switches[9]. However, interfacing the nanometer sized molecular system with outside circuitry stays as a challenging obstacle for expanding the application of these nano-scale electronic components. In this paper, we developed a molecular system that can be easily interfaced with and can be readily integrated with conventional CMOS circuitry. We used self-assembled monolayer and multilayers of pyryl phosphonic acid to achieve this goal. Formation of high quality SAMs with good coverage on silicon dioxide surface using molecules with phosphonic acid termini have been previously studied[10-12]. Silicon dioxide is a surface that is accessible after the completion of a CMOS microfabrication process thus our proposed molecular system can be integrated with CMOS circuitry as an easy post-processing step.

Our proposed structure consists of an array of interdigitated metal electrodes on silicon dioxide. We form

the SAM of pyryl phosphonic acid between the electrodes to construct the lateral conduction channel. The height of the channel is equal to the height of the molecules constituting the SAM (~ 0.9 nm) shown as Figure 1. By varying the conjugated group that is attached to the phosphonic acid termini, the potential landscape in the channel can be engineered with nano-scale precision.

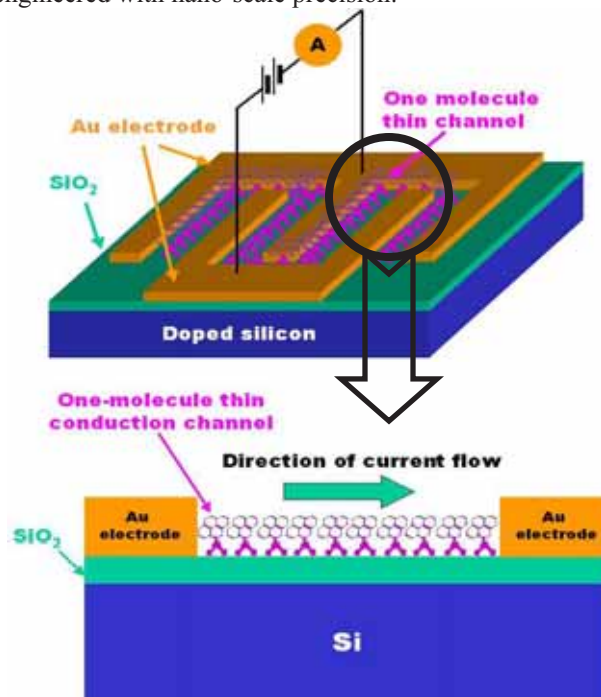


Figure 1: 3-D view of a lateral carrier transport channel made via self-assembly of conjugated molecules (top) and the detailed schematic showing the current flow through the one molecule thin SAM across the patterned electrodes (bottom).

Fabrication of the microelectrodes

Fabrication process of the microelectrodes included one e-beam lithography and one metal evaporation followed by liftoff in acetone to define the 200 nm wide electrodes and their contact pads.

The electrode fabrication started from a single-side polished 3” wafer (Ultrasil Corp., Sb doped, 0.01~0.02 Ω ·cm resistivity, 1-0-0). We first grew a 200 nm thick thermal dry oxide over the silicon wafer for assembling the PYPA monolayer. We then diced the wafer into 2.5 cm x 1 cm

chips followed by extensively cleaning the chips with acetone, isopropanol rinse and 30 minutes oxygen plasma treatment. We spincoated a ~200 nm thick polymethyl methacrylate (PMMA) layer on the chip using 3% 950PMMA A anisole solution (Microchem Corp., Newton, MA) at 1,500 rpm. We created microelectrodes pattern using DesignCAD LT 2000 software (Upperspace Corp., Pryor, OK) embedded with the Nanometer Pattern Generation System (NPGS) (JC Nability Lithography Systems, Bozeman, MA). Each electrode has 50 10 μm long and 200 nm wide fingers and one 250 \times 100 μm^2 contacting pad. The nominal gap between the adjacent fingers is 200 nm. Following the pattern created by software, we selectively exposed the PMMA layer with a Siron XL30 scanning electron microscope (SEM) (FEI Company, Hillsboro, OR) and developed the pattern using 1:3 methyl isobutyl ketone (MIBK) to isopropanol mixture. The chip with the defined PMMA patterns is then baked at 95°C to remove the residual solvent and moisture.

Using a CV-18 resistance evaporator (Consolidated Vacuum Corp., Rochester, NY), we evaporated a 5 nm thick chromium adhesion layer followed by a ~50 nm thick gold layer. We left the chip in acetone overnight and then sonicated the chip in acetone bath for 20 minute to ensure the complete removal of unwanted metal layers. After the fabrication of the microelectrodes, we used SEM and atomic force microscope (AFM) to check the integrity of the fabricated devices. Figure 2 shows the SEM picture of a pair of fabricated electrodes.

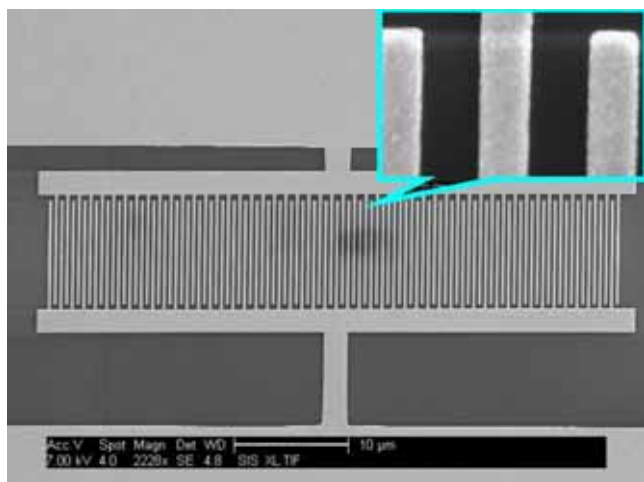


Figure 2: Scanning electron microscope picture of the interdigitated electrodes fabricated on SiO₂/Si surface.

Formation of self-assembled monolayer and multilayer

Figure 3 shows the synthesis procedure of PYPA. This molecule contains two groups with distinct chemical properties. The polar phosphonic acid group forms the covalent phospho-silano diester bond with the silicon dioxide surface while the conjugated pyrene group forms the conducting channel via π - π stacking. Diethyl 3-pyrylphosphonate was prepared via the lithiation of 1-

bromopyrene at -78°C followed by the nucleophilic attacking on diethyl chlorophosphate. The reaction of diethyl 1-pyrylphosphonate with bromotrimethylsilane generated di(trimethylsilyl) 1-pyrylphosphonate which was hydrolyzed with water to afford 1-pyrylphosphonic acid.

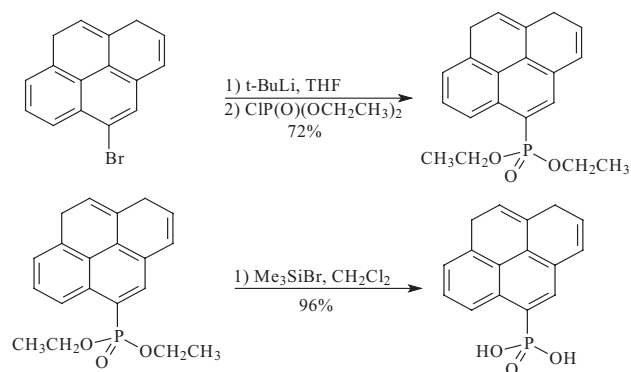


Figure 3: Synthesis schematic of pyryl phosphonic acid (PYPA) from 1-bromopyrene.

During the assembly of the PYPA SAM, we spotted 30 μL 1.0 mM ethanol solution of PYPA on the chip with metal electrodes and let the solution sit on the chip for 60 seconds followed by spincoating at 1,500 rpm. Then the chip is heated in a vacuum oven at 170°C for 9 hrs to promote the formation of the phospho-silano diester bond. After rinsing the chip with ethanol, a single molecule thick PYPA SAM was formed. However, skipping the heating step allows the self-assembly of PYPA at room temperature to create micro-domain sized PYPA crystalline multilayer.

After completing the formation of PYPA SAM and multilayer on the chip, we characterized them by atomic force microscope (AFM) and x-ray photoelectron spectroscopy (XPS). Figure 4 shows AFM pictures of the formed SAM and multilayer. AFM studies revealed that height of SAM is 0.9 nm while the height of a multilayer is a multiple of 2.5 nm.

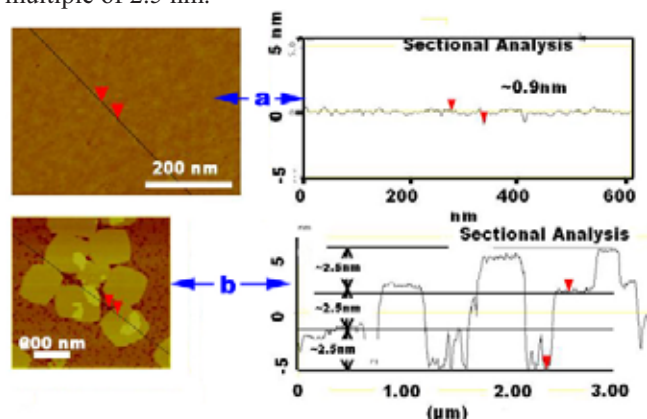


Figure 4: a) AFM section analysis of PYPA SAM deposited on SiO₂/Si and b) AFM sectional analysis of PYPA multilayer on SiO₂/Si.

We also performed the scanning tunneling microscopy (STM) on the PYPA multilayer deposited on Au surface.

Results shown in Figure 5 disclosed the alignment of the molecule, which can have a significant positive impact on the effective charge mobility in this system.

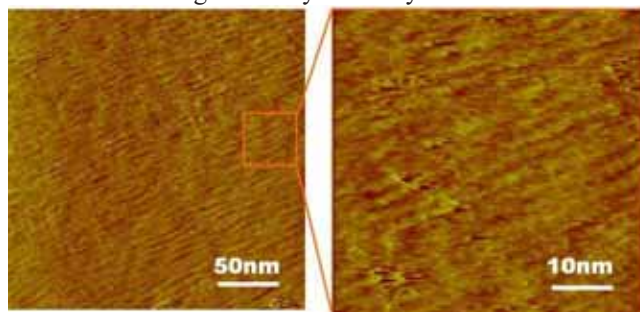


Figure 5: STM picture of the PYPA multilayer deposited on gold surface.

Figure 6 summarizes our argument for observing 2.5 nm step size in the multilayer. This observation is primarily due to intermolecular π - π stacking and hydrogen bond interaction between the phosphonic acid moieties in PYPA.

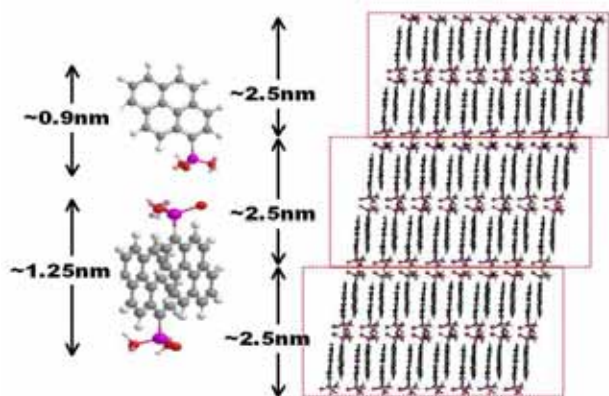


Figure 6: Proposed double bilayer unit model forming PYPA multilayer crystalline structure based on the AFM results shown in Figure 4b.

Table I shows the XPS results on control sample, PYPA SAM and PYPA multilayer samples. Higher carbon composition as well as lower silicon and oxygen compositions on the chip with PYPA SAM implied the existence of organic thin layer on these chips. Much higher carbon composition and the presence of phosphorus element in the multilayer sample further suggested the existence of a thicker layer comprised of PYPA molecules.

	C	O	Si	P
Control	9.03	61.23	29.7	N/d
PYPA SAM	17.77	53.47	28.1	N/d
PYPA multilayer	71.77	16.97	4.5	3.77

Table I. Atomic percentage composition as determined by XPS for control SiO₂, PYPA SAM and PYPA multilayer samples.

Characterization of the electrical properties of the channels

We carried out the current-voltage (I-V) curve measurements of the fabricated channel of both SAM and multilayer. These measurements were performed using a Keithley 6430 remote sourcemeter (Keithley Instruments Inc., Cleveland, OH) with a DesertCryogenic probe station (Desert Cryogenics, Tucson, AZ). All measurements were carried out under vacuum ($<2.0 \times 10^{-6}$ bar). The automatic current sampling software was written using Labview 6.0 program (National Instruments Corp., Austin, TX).

For making each I-V curve, voltage was swept from -2V to 2V with 0.1V interval. I-V curves of at least five devices were measured to ensure the duplicability. Figure 6 shows the plot of the averaged I-V curve measured at 300°K from five devices with error bars. This curve shows a voltage dependence of

$$I \propto e^{B\sqrt{V}}$$

indicating a shallow trap dominant conduction[13, 14].

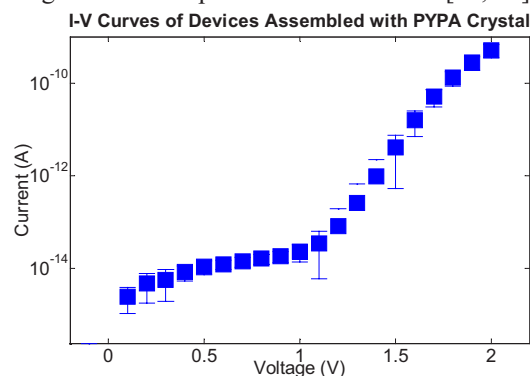


Figure 7: I-V curve of the PYPA multilayer devices at 300°K under 3×10^{-7} torr vacuum.

We also measured the currents at temperatures varied from 170°K to 310°K at fixed bias of 2V shown as Figure 8 and fit this curve with an Arrhenius equation which led to the finding of a 0.326eV activation energy of the traps. To find the carrier mobility in the PYPA multilayer, gating effect studies of FET made of PYPA multilayer are in progress.

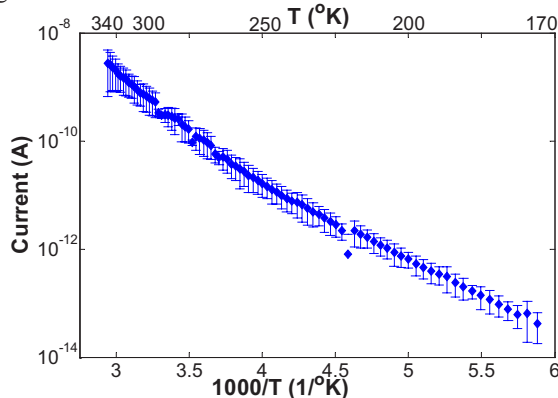


Figure 8: Dependence of current flowing through PYPA multilayer on temperature at 2V bias and 3×10^{-7} torr vacuum.

Discussions

Besides studying the electrical conduction through the PYPA multilayer, we also investigated the conduction through the PYPA SAM. However, at varied measurement temperatures and pressure, we have not found current through the devices with SAM higher than the leakage current in the control devices (Results not shown). To understand the dissimilar conduction behavior between PYPA SAM and multilayer, we used AFM to find the structure of PYPA micro-domain sized crystal before and after the heating at 170°C that promotes the bond formation between the phosphonic acid group and silicon dioxide surface. What we found indicated that at high temperature, the PYPA crystals were disintegrated into islanded or amorphous layers. Moreover, the amorphousness of the silicon dioxide surface renders it difficult for the covalently bonded PYPA SAM to maintain a long-range ordered packing. While, previous work on pentacene showed that order and grain size of the pentacene crystals was important to achieve high mobility in pentacene thin film transistor devices[15]. Recently, it was also found that conduction through a SAM FET made of a tetracene derivative formed on Al₂O₃ substrate diminished as the distance between drain and source spans more than one Al₂O₃ grain[16]. Both results suggested that the boundary of polycrystalline domains caused significant deterioration of conduction and long-range packing of molecules is important to the conduction through the SAM on silicon dioxide. There are two approaches that could improve the packing of a monolayer on the oxide surface. We can either form SAM on an oxide with proper crystalline orientation such as TiO₂, Al₂O₃ or SrTiO₃ or chemically crosslink the molecules forming the monolayer to force order packing within the monolayer. Both approaches are under investigation in our research group.

Acknowledgements

We are indebted to the Nanotechnology User Facility at the University of Washington for its assistance in electron beam lithography and scanning electron microscopy. JD thanks the Nanotechnology Fellowship sponsored by the University Initiative Fund (UIF) for partially funding this research.

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