Electrochemical Deposition of Polyaniline on Nanoelectrode CrossBar Structures

Jose Guevarra

Mechanical Engineering, University of California, Santa Barbara

NNIN iREU Site: Institut Für Bio- Und Nanosysteme (IBN), Forschungszentrum, Jülich, Germany

NNIN iREU Principal Investigator(s): Dr. Dirk Mayer, Molecular Bioelectronics, Forschungszentrum, Julich

NNIN iREU Mentor(s): Nils Sanetra, Molecular Bioelectronics, Forschungszentrum, Julich

Contact: joseg@engineering.ucsb.edu, dirk.mayer@fz-juelich.de, n.sanetra@fz-juelich.de

Abstract:

Molecular bioelectronics investigates the electronic characteristics of biomolecules, hoping to replace conventional electronic components with molecular equivalents, and produce new biosensors. Molecular electronics typically interacts with layered and even single biomolecules by metallic electrodes. Fabricating electrodes separated by a gap size comparable to the size of molecules is difficult. A convenient method of filling this space is to electrochemically deposit conducting material on the electrodes to fill the gap. Polyaniline (PANI) was electrochemically deposited on nanoelectrodes to bridge the gap between two parallel 300 nm half-pitch gold (Au) electrodes. By varying the deposition time, voltage bias, and aniline monomer concentration several different PANI morphologies were produced.

Introduction:

Molecular bioelectronics integrates biomolecules into inorganic structures in order to investigate and control charge transport phenomena in and across biomolecules. An increasingly helpful tool in investigating biomolecules electronic properties is the crossbar electrode structure. Created by intersecting nanoscale electrodes, one on top of the other, crossbar electrodes have an interjunction gap that can be filled with monolayers or individual biomolecules. Fabricating electrodes separated by tens of nanometers is difficult. A method of producing a gap size on the order of molecules is to electrochemically deposit conducting material between the electrodes. The aim of this project was to investigate if PANI could be used to bridge the gap between two parallel 300 nm half-pitch electrodes.

Aniline is an organic compound that can be oxidized into a conducting polymer, emeraldine. By applying a voltage bias between two electrodes immersed in an aniline monomer electrolyte, the aniline oxidizes on the cathode thus depositing polyaniline (emeraldine) on the electrode. As the PANI grows out from the electrode, it creates an electrically conductive "bridge" in the gap between the parallel electrodes.

Experimental Procedure:

A 0.1M aniline + 0.5M H_2SO_4 solution was made by mixing aniline monomer (Sigma-Aldridge) and sulfuric acid (H_2SO_4) in water. Aniline monomer instantly precipitates when added to H_2SO_4 solution. Shaking the mixture dissolves the precipitate.

The current between parallel electrodes was tested in air to ensure that they were not electrically connected. A micropipette was used to directly apply a drop of aniline solution onto the electrodes, then a voltage bias is applied across the electrodes for over an hour using a probe station. After the deposition was performed, the electrodes were cleaned in Milli-Q water, blown dry, and cyclic voltammetry was performed on the electrodes immersed in H_2SO_4 and in air to test their conductance. Several different voltage biases (0.95V, 0.97V, 1V) and doubling the aniline concentration were used to observe their effect on the deposition.

Results:

After the electrodeposition, a green substance was observed on the acting cathode, Figure 1. Due to the nanoscale gap

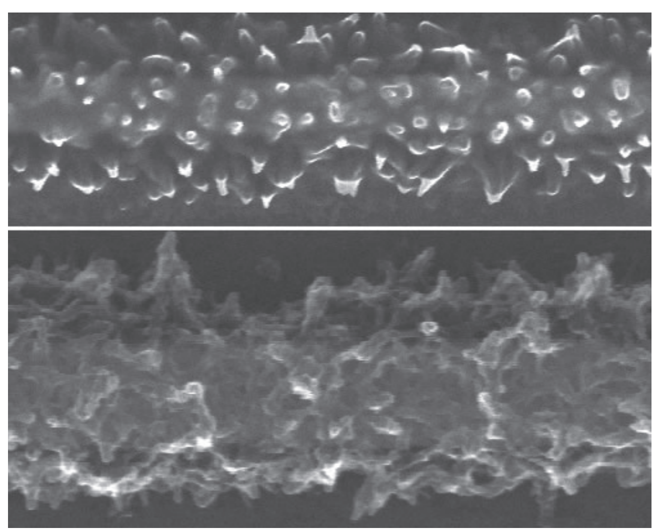

Figure 1: Depositions using 0.1M aniline (top) and 0.2M aniline (bottom) solutions.

Figure 2: Parallel electrodes before the deposition of polyaniline (top) and after (bottom).

between the electrodes, it was not possible to observe if bridging between the gap had occurred with a microscope; bridging could be determined several other ways. During the deposition, the conductance would fluctuate and increase in a step-like fashion due to PANI reaching the other electrode, hence allowing current to pass between the electrodes. After rinsing the electrodes in water and blowing them dry, a voltage sweep in air could also be performed to compare the conductance before and after the deposition. The conductance ranges on the order of 10^{-8} to 10^{-6} S in air. The PANI growth between the electrodes could also be viewed by using a scanning electron microscope (SEM). Figure 2 shows an SEM image of the space between two parallel electrodes. It shows small protrusions from the cathode (bottom) crossing the gap and contacting the other electrode. By varying several parameters of the electrochemical deposition, the morphology of the deposited PANI could be changed.

The electrochemically deposited PANI has a coral-like morphology. An increase in the concentration of the aniline monomer has a tendency to decrease the emeraldine density and change the emeraldine morphology. Figure 3 shows a deposition performed using 0.1M aniline + 0.5M H_2SO_4 (top) and another performed using double the aniline concentration (bottom).

Three different voltage biases were used to deposit PANI on Au electrodes. Increasing the voltage bias had a tendency to decrease the deposition density over the electrodes. Figure 4 shows the PANI morphology for biases of 0.95V, 0.97V, and 1V (top to bottom). The coral-like features of the PANI decrease as the voltage is increased despite having similar deposition times and aniline concentrations. This may be due to oxidation of emeraldine occurring at lower voltages.

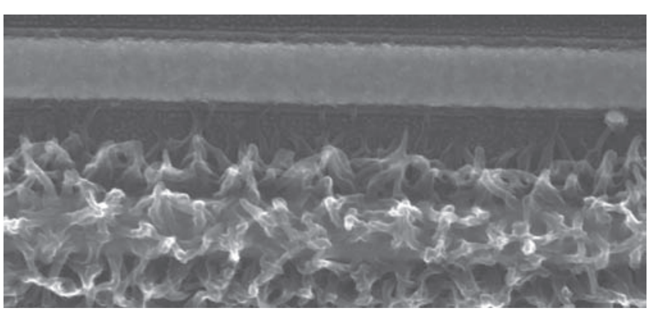

Figure 3, left: Emeraldine protrusion connecting the cathode to the anode across a 300 nm gap.

Conclusions:

The conducting polymer emeraldine was electrochemically deposited on Au electrodes. The morphology of the PANI can be modified by changing the aniline concentration or the voltage bias. The time required to bridge the 300 nm gap between electrodes ranged from 45 minutes to 1.5 hours. The expected conductance after bridging occurs ranges from 10^{-8} to 10^{-6} S when measured in air.

Future Work:

Deposition results vary with aniline concentration and solution immersed electrode surface area. To control these parameters applying a funnel structure over the electrodes is recommended. Future work will consist of applying top electrodes on polyaniline deposited bottom electrodes, measuring the resulting conductance between top and bottom electrodes, and depositing biomolecules between the interjunction gaps.

Acknowledgments:

The National Nanotechnology Infrastructure Network, The National Science Foundation, Lurie Nanofabrication Laboratory. I would like to thank Dr. Dirk Mayer, Dr. Andreas Offenhäusser, and Niles Sanetra for their guidance and help with my project. Thanks to everyone at IBN-2, Lynn Rathbun, and my fellow REU students for their motivation and making the summer such a great experience.

References:

[1] Staikov, G; "Electrochemical formation and the properties of thin polyaniline films on Au (101) and p-Si (111)"; Appl. Phys, A 87,405-409 (2007).

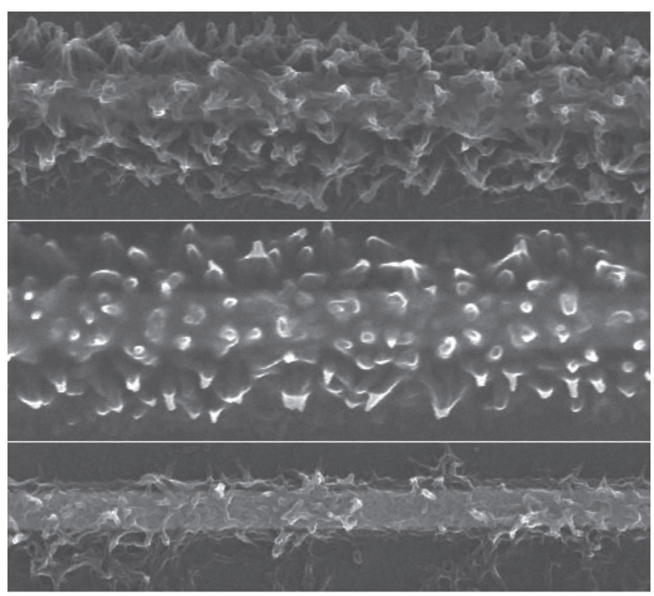

Figure 4, above: Depositions performed at 0.95V (top), 0.97V (center), and 1.0V (bottom).