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**ELECTROCHEMICALLY-FABRICATED METAL NANOSTRUCTURES FOR
SENSING, RESISTIVE SWITCHING, RAMAN ENHANCEMENT, AND
MAKING CONTACT TO MOLECULAR JUNCTIONS**

By

Radhika Dasari

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for the Degree of

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University of Louisville
Louisville, Kentucky

August 2011

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Dedicated to my Parents

Latha Dasari and Keshava Reddy Dasari

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ABSTRACT

ELECTROCHEMICALLY-FABRICATED METAL NANOSTRUCTURES FOR SENSING, RESISTIVE SWITCHING, RAMAN ENHANCEMENT, AND MAKING CONTACT TO MOLECULAR JUNCTIONS

RADHIKA DASARI

(AUGUST 03 2011)

The research in this dissertation describes a simple electrochemical approach for fabricating nanoscale (metal/metal) or molecular (metal/polymer or self assembled monolayer (SAM)/metal) junctions. The fabrication involves metal deposition on one set of electrodes (E1), where the metal grows and becomes connected to a second set of electrodes (E2) of an Au interdigitated array of electrodes with a 5 μm separation. The fabrication of molecular junctions involves deposition of a thin polymer or self assembled monolayer film on one set of electrodes (E2) prior to metal deposition on the other set of electrodes (E1). The method is simple, low cost, highly parallel, and applicable to a wide variety of molecules and thin films with interesting electronic properties.

Different metal/metal and metal/molecule or polymer/metal junctions such as E1/nano Pd/E2, E1/nano Pd/polyphenol/E2, E1/Ag nanowire(NW)/E2, E1/AgNW/polyphenol/E2 and E1/AgNW/SAM/E2 junctions were fabricated using this

electrochemical approach. The H₂ sensing properties of E1/nano Pd/E2, E1/nano Pd/polyphenol/E2, and E1/AgNW/polyphenol/E2 functionalized with Pd nanoparticles were explored. E1/nano Pd/polyphenol/E2 junctions behaved as H₂ switches above 1% H₂ (10⁷ on/off ratio) while E1/nano Pd/E2 and E1/Ag NW/polyphenol/E2 functionalized with Pd nanoparticles behaved as H₂ sensors and detected H₂ gas rapidly and reversibly down to 0.11%.

The resistance of E1/AgNW/polyphenol/E2 junctions was controlled by electrodepositing polyphenol of different densities within the junction. This procedure did not lead to precise control over the resistance, but the number of polyphenol electrochemical cycles used during the synthesis did offer some general control over the resistance over 9 orders of magnitude. For E1/AgNW/SAM/E2 junctions, where the SAM is comprised of alkanethiols, the resistance generally depends on the length of the alkane chain within the junction from C4 to C18. While the resistance was still not precisely controlled, the % of short circuits between the Ag NW and the E2 electrode decreases as the chain length of the SAM increases. This approach is useful for device fabrication, but better reproducibility is required for fundamental molecular electronics studies.

The electrochemically deposited Ag NW contacts significantly enhance the Raman scattering signals for aminothiophenol (ATP) molecules in E1/AgNW/ATP/E2 junctions. The extent of surface enhanced Raman spectroscopy (SERS) enhancement at several junctions within a device depends on the contact between the AgNW and ATP SAM coated electrode. The SERS enhancement was estimated to be 10⁶ – 10⁸, which was large enough to detect submonolayer coverages of ATP molecules diluted by a factor

of 1000 with hexanethiol molecules. E1/AgNW/ATP/E2 junctions are useful as a platform for performing simultaneous conductivity and SERS measurements to correlate the electronic properties of molecules within the junction to its structural properties. E1/AgNW/E2 junctions with the AgNW/E2 contact broken electrochemically behave as resistance switching devices. These Ag filament-based switching devices exhibited reversible switching with an on/off ratio over 10^4 and endurance of at least 100 cycles.

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CHAPTER I

INTRODUCTION

1.1. Main Goal/Summary:

The main goal of this research was to develop an electrochemical method to fabricate electronic devices comprising metal nanostructures, molecules, and thin polymer films as the basic components in a fast, reliable and reproducible manner and to use them for several applications such as sensing, molecular electronics, and enhanced Raman spectroscopy. Metal nanostructure based devices were fabricated by electrodepositing metal on a pair of contact electrodes. Molecule-based devices were fabricated by depositing a molecular or polymer film on one electrode and metal on a second nearby electrode.

This dissertation is divided into five main parts. Chapter I is the introduction and Chapter II describes the experimental procedures for the fabrication of metal/metal and metal/molecule or polymer/metal junctions. Chapter III describes an electrochemical method for fabricating electrode (E1)/nano Pd/electrode (E2) and E1/nano Pd/polyphenol/E2 junctions. Here we explored the H₂ sensing characteristics of both junctions. In Chapter IV we describe the fabrication of junctions with Ag nanowires (NWs) contacted to self assembled monolayers (SAMs) and polyphenol. Ag deposited in the form of nanowires, unlike Pd, which deposited as dendritic structures. We also demonstrated the application of E1/Ag nanowire (AgNW)/polyphenol/E2 junctions functionalized with Pd nanoparticles for H₂ sensing. Chapter V describes a method for

fabricating two terminal resistive switching devices using Ag NWs electrodeposited across micron gap electrodes. Chapter VI describes surface enhanced Raman spectroscopy (SERS) at E1/AgNW/SAM/E2 junctions specifically with aminothiophenol (ATP) within the junction. Chapter VII describes simultaneous conductivity and SERS measurements at E1/AgNW/ATP/E2 junctions and Chapter VIII includes a summary and conclusions.

1.2. Motivation/Objective:

The majority of this work was motivated by the need to develop a simple, fast, and reliable method for the fabrication of different functional electronic devices using metal nanostructures, molecules, and polymer films as the basic components. That way we can spread this research out and also undergraduate research institutes can use this approach to fabricate different functional electronic devices. The fabrication of molecule and polymer based electronic devices will avoid the size limitations associated with current silicon based technology. Also the ultimate limit of detection for analytes could be achieved by fabricating single molecule electronic sensing devices. Developing simple, reproducible methods for fabricating these types of devices would allow a variety of devices to be studied fundamentally and tested for different applications. Simple approaches could allow for a broad range of scientists to enter the field and make it possible to obtain reliable, statistical measurements of devices.

1.3. Importance of nanostructures:

Nanostructures made up of metal, semiconducting, and carbon materials have gained enormous interest in recent years. As the size of a material is reduced to the nanoregime, there is an increase in surface-to-volume ratio that leads to very interesting optical,¹⁻²

catalytic,³⁻⁶ electrochemical,⁷⁻¹⁴ thermal,¹⁵ and electronic¹⁶⁻¹⁷ properties that are different from their bulk counterparts. Metal nanostructures, especially, are of great importance as they exhibit very interesting and new phenomena. A few examples include size dependent excitation or emission,¹⁸⁻¹⁹ quantized conductance,²⁰ Coulomb blockade,²¹ and metal-insulator transition.²² As these nanomaterials possess fascinating properties, they can be used for several applications, such as fluorescence,²³ waveguides,²⁴ therapeutics,²⁵ surface-enhanced Raman spectroscopy,²⁶ and sensing.²⁷ Materials constrained to less than 100 nm in one dimension are called one-dimensional nanostructures. One-dimensional nanostructures are especially attractive as they can be used as electronic interconnectors and functional units in nanoscale electronic, optoelectronic, electrochemical, and electromechanical devices with nanoscale dimensions.²⁸

1.4. Synthesis of one dimensional metal nanostructures:

In Chapters III and VII, we describe an electrochemical method to synthesize one dimensional metal nanostructures spanning micron gap electrodes. There are several other impressive synthetic methods that exist to make such nanostructures. In general, the synthesis involves a metal ion precursor (M^{n+}) which is reduced to M^0 in the presence of a shape-inducing agent. These shape-inducing agents could be either soft templates or hard templates. Therefore, synthetic methods can be generally classified into so-called soft-template and hard-template approaches. One dimensional metal nanostructure synthesis in soft and hard templates have been reviewed by several authors.²⁹⁻³²

Chemical Soft-template methods: In soft-template or solution phase synthesis, the metal precursor is reduced in the presence of structure directing molecules such as surfactants, polymers, or ionic species. These structure directing molecules either inhibit

the growth of certain metallic crystals or alter the transport of reagents to certain crystall faces. Cylindrical micelles,³³ block copolymers,³⁴ DNA molecules,³⁵ and cetyltrimethylammonium bromide (CTAB)³⁶⁻³⁸ surfactant are a few examples of soft-templates. Figure 1.1 shows a schematic representation of the blockage of Au (100) crystal faces by cetyltrimethylammonium bromide, promoting growth along (111) faces to form 1D nanorods.

Chemical Hard-template methods: In the hard template method, the growth of the nanostructure is confined within a hard template. Usually an inorganic material or polymer, typically in the form of a porous membrane serves as a template. Nanoscale channels in polycarbonate and alumina membranes are the most widely used templates.³⁹⁻

⁴⁰ Chemical methods for reduction of metal ions in hard templates have been reported.

1.4.1. Electrochemical synthesis of 1D Metal Nanostructures:

Electrochemical methods of synthesis are very promising and versatile as a wide variety of materials such as metals, metal oxides, alloys, and polymers can be electrodeposited. The combination of electrodeposition with large scale integrated microfluidic networks has the potential for producing nanowire arrays.⁴¹ An electrochemical method developed by us to synthesize metal nanostructures across a microgap electrode devices is described in Chapters III-VII. Hence a few examples of electrochemical methods utilizing soft and hard templates for forming 1D nanostructures are provided.

Electrochemical methods for synthesizing 1D nanostructures in soft and hard-templates have been reported by several groups.⁴² As with chemical synthesis these can be separated into soft and hard template methods as described next.

Figure 1.1. Schematic representation showing the blockage of Au (100) crystal faces by cetyltrimethylammonium bromide (CTAB).

Electrochemical Synthesis of 1D nanostructures using soft-templates: Several groups reported an electrochemical method for the synthesis of 1D Au nanostructures in aqueous solution in the presence of capping agents.³⁶⁻³⁸ In general, a two electrode setup is used where a Au plate is the anode and a platinum plate is the cathode.

Cetyltrimethylammonium bromide (CTAB) surfactant was used as the capping agent, and it preserves the shape and stabilize the nanostructures. Tetradodecylammonium bromide (TCAB), a more hydrophobic cationic co-surfactant, can also serve as a “shape-inducing” reagent.

Electrochemical synthesis of 1D nanostructures using hard-templates: Martin and co-workers were the first to use porous membranes (polycarbonate or alumina) in the synthesis of metal and polymer tubules, rods, and wires by electrochemical deposition. Membranes with different pore ranges and densities are commercially available. The diameter of the nanostructure was determined by the diameter of the membrane pore where as the length of the nanostructure was determined by the thickness of the membrane. Thus, nanostructures of different aspect ratio can be formed by controlling these two parameters of the membrane. Figure 1.2A shows a schematic representation of the steps involved in the synthesis of 1D metal nanostructures using a polycarbonate membrane as a template.

Penner’s group fabricated nanowires by electrodeposition of metals and metal oxides at the step edges of a highly oriented pyrolytic graphite (HOPG) surface. Because step edges serve as defect sites, it is energetically favorable for the electrochemically formed metal atom to attach itself to the step edges. The proper deposition potential to confine the nucleation to the edges is determined by obtaining a cyclic voltammogram of a

Figure 1.2. Examples of the hard templates used for 1D nanostructure synthesis. (A) Porous polycarbonate membrane and (B) Highly oriented pyrolytic graphite (HOPG).

HOPG surface in a solution of the metal ion of interest. These nuclei grow into nanostructures and fill up the step edges. With an increase in the deposition overpotential, the selectivity of nucleation on the surface and the distribution of the nanowires changes dramatically. Hence, by controlling the magnitude of the overpotential, the selectivity of nucleation on the edge sites and the distribution of the NWs on the graphite surface can be controlled. The morphology of the nanostructures is determined by the morphology of the step edges. Figure 1.2B shows a schematic representation of the synthesis of 1D metal nanostructures using HOPG as a template.

The above described methods are great for controlling the synthesis of 1D metal nanostructures, but they also suffer from several issues. Nanostructures have to be assembled on surfaces to fabricate an electronic device. In solution-based methods, aggregation of nanostructures, uncontrolled placement of nanostructures on surfaces, and the need to remove impurities are some of the concerns in post-synthesis assembly of nanostructures on surfaces from solution. In template based methods, the template has to be removed by chemical etching in order to harvest the resultant nanostructures, which then have to be assembled on a surface.

1.4.2. Fabrication of an electronic device using 1D nanostructures:

To fabricate an electronic device using 1D nanostructures, the structures need to be assembled on an insulating surface and electrical contacts have to be made to the nanostructures. Various strategies have been reported in the literature for fabricating contacts to nano-materials in nanoelectronic devices. These strategies can be generally classified into the following two methods.

1.4.2A Contacts after: Assemble 1D nanostructures on a surface first and then make

electrical contacts (see Figure 1.3 A).

1.4.2B. Contacts before: Fabricate contacts on a surface first and then assemble or grow nanostructures across the contacts (see Figure 1.3 B).

1.4.2A. Contacts after: A few examples where contacts were made after 1D synthesis are as follows:

Electron-beam lithography is the most common method to make contacts, but it is expensive and tedious.⁴³⁻⁴⁴ Ag paint can also be applied to metal nanowires as contacts as demonstrated by Penner and co workers, who electrochemically deposited Pd mesowire arrays on HOPG, transferred them onto a cyanoacrylate film supported on a glass slide, and applied Ag paint manually to the ends of the mesowires.⁴⁵

1.4.2B. Contact before: Here, contacts (electrodes) are prefabricated first and later either nanostructures are assembled or grown across the contacts.

1.4.2B1. Nanostructures assembled on prefabricated electrodes: Several methods to assemble nanostructures on lithographically prefabricated electrodes are reported in the literature.

- **Mechanical positioning:** Nanostructures are placed between the two electrodes using atomic force microscopy.⁴⁶
- **Electric field assisted assembly:** An electric field is applied to position individual nanowires between two electrodes from colloidal suspensions.⁴⁷
- **Dropcast:** A solution of nanostructures is dropcast deposited on the surface to place the nanostructures between the electrodes.⁴⁸

Contacts formed using the above techniques are not very reproducible and often have

Figure 1.3. Schematic representation showing the fabrication of contacts to 1D nanostructures. (A) Contacts after and (B) Contacts before.

high resistance. Some strategies involve multiple steps and are time consuming. Time consuming and tedious postgrowth device assembly can be eliminated by growing the nanowires directly between prefabricated electrodes, which is the strategy we use in this dissertation.

1.4.2B2. Nanostructures grown directly on prefabricated electrodes: Several different methods to grow nanostructures directly at prefabricated electrodes exist.

- **In-situ electric field:** Dai et al. used in-situ electric fields to grow SWNTs onto surfaces by CVD.⁴⁹
- **Field emission:** Velev and co workers used field emission in a low-pressure tungsten carbonyl atmosphere to grow single tungsten nanowires across two bare metal electrodes.⁵⁰
- **Electrochemical methods to grow nanostructures across prefabricated electrodes:** In Chapter II-VII, we describe an electrochemical method for growing nanostructures across prefabricated electrodes. Other groups also electrodeposited nanostructures across prefabricated electrodes. These are discussed in detail in the following section.

1.4.3. Electrochemical methods to grow nanostructures across the prefabricated electrodes: Tao and coworkers fabricated stable copper nanowires across prefabricated Au electrodes using an electrochemical method.⁵¹ Au electrodes of ~ 100 nm were fabricated on oxidized Si substrates by combining photolithography and focused ion beam techniques. In order to eliminate the ionic conduction in the etching/deposition, (CuSO₄) these Au electrodes were covered with a Si₃N₄ insulation layer. Conductance

between the electrodes was monitored continuously during the deposition. With a feedback circuit, deposition was controlled until a desired conductance was reached. When the nanowire was overgrown, the feedback circuit switched on the etching process in order to decrease the conductance to the desired value.

Penner and coworkers reported an electrochemical method to grow single Pd and polypyrrole wires across prefabricated electrodes using e-beam lithography patterned electrolyte channels.⁴⁴ A Si wafer was cleaned using standard RCA. Low-pressure chemical vapor deposition was used to deposit a 1 μm thick Si_3N_4 layer on the Si wafer. Later a Ti adhesion layer was deposited followed by deposition of $\sim 3000 \text{ \AA}$ thick Au contact layer. Au contacts were patterned by lift-off. SiO_x was then deposited on the wafer using a thermal evaporation method. E-beam lithography was used to open the SiO_x to form the electrolyte channel. A micropipette was used to place the electroplating solution in the channel and an electric potential was applied to grow the wire from the cathode to the anode through the channel.

Haynie and coworkers reported a method for assembling Pd nanowires between microgap electrodes from a palladium acetate solution.⁵² An alternating electric field of relatively high intensity and frequency was applied to the electrodes in the palladium deposition solution. The concentration of palladium acetate, applied voltage, and frequency were the factors that affect the nanowire formation.

In the above three methods, nanowires were electrodeposited directly across the electrodes. We also electrodeposited Pd nanostructures and Ag NWs across prefabricated electrode devices as described in Chapters II-VII. Most previous studies involve some type of ion-beam or e-beam lithography, which is tedious and costly. Our approach and

Haynie uses electrodes fabricated by photolithography, which can be achieved at lower cost and in a highly parallel manner. Our approach is beneficial as it is simple and versatile, since we can quickly prepare nanowire contacts to any metal, metal oxide or polymer that can be electrodeposited. Chapters II-VII describe the electrodeposition of Pd nanostructures and Ag NWs across 5 micron gap Au electrodes for applications in sensing and molecular electronics.

1.5. Importance of molecular electronics:

In Chapter II, III, IV, VI and VII, we describe an electrochemical method to fabricate molecule and polymer based electronic devices. In general, a molecular electronic device consists of a single molecule, monolayer of molecules, or multilayer film of molecules sandwiched between two contact electrodes. Figure 1.4 shows a schematic representation of different types of molecular electronic devices. It has been demonstrated that the properties of individual, small groups, or thin films of molecules are useful for electronic and photoelectronic-based devices, such as switches and sensors. Molecule-based electronic devices have been heavily explored in recent years as this approach may someday overcome the size limitations of the current silicon based electronics technology. It is possible to fabricate a wide variety of functional devices using molecules based on their electronic, optical, magnetic, thermoelectronic and molecular recognition properties. Understanding the electronic properties of molecules is essential to fabricate future molecule-based devices. It is therefore necessary to easily and reproducibly prepare metal/molecule/metal junctions in order to study the fundamental electronic and structural properties of the molecules within the junction.

1.5.1. Methods to form Metal/Molecule/Metal junctions:

Single molecule

Monolayer of molecules

Multi layer (film)

Figure 1.4. Schematic representation of different types of molecular electronic devices.

Various techniques have been used for fabricating and studying the electronic properties of metal/molecule/metal junctions. These techniques can be generally classified into one of the following two methods.

1.5.1A. Contacts before: Here molecules are assembled between prefabricated nanogap electrodes.

1.5.1B. Contacts after: Molecules or films are deposited on one electrode and then a second electrode is brought into contact with the molecule.

1.5.1A. Contacts before: Molecules have been assembled between pre-formed nanogap electrodes to form metal/molecule/metal junctions (see Figure 1.5). Electromigration formed break junctions,⁵³⁻⁵⁵ mechanically controlled break junctions,⁵⁶⁻⁵⁸ optical lithography,⁵⁹ and molecular lithography⁶⁰ are examples of techniques used to fabricate nano-gap electrodes. All of these approaches are somewhat tedious, have low yields, and lack reproducibility. Electrochemical methods to make nanogap electrodes are discussed in the following section as these are most relevant to our research.

1.5.1A1. Electrochemical methods to make nanogap electrodes: Molecules have been assembled between nanogap electrodes fabricated electrochemically using the methods termed on-wire lithography (OWL)⁶¹ and nanowire lithography.⁶² In OWL and nanowire lithography a porous alumina membrane was used as a template and different metals were electrochemically deposited into the membrane pores to synthesize multisegmented nanowires. One of the metals acts as a sacrificial layer and is removed by selective wet-chemical etching to create a nanogap. These approaches require assembly and electrical contact after formation of the molecular junctions. Tao and coworkers developed an electrochemical deposition/etching method to fabricate

Figure 1.5. Schematic representation showing the assembly of molecules between prefabricated nanogap electrodes (contacts before).

atomic or molecular scale nanogap electrodes and studied the sensing and electronic properties of polymers in the gap.⁶³⁻⁶⁶

1.5.1B. Contacts after: Here molecules or thin films are deposited on one electrode and then the second electrode is brought into contact with the molecules. The second electrode is then brought into contact with molecules either physically or by deposition.

1.5.1B1. Physical methods: Scanning probe microscopy (SPM) methods, such as scanning tunneling microscopy (STM)⁶⁷⁻⁷³ and conducting tip atomic force microscopy (CT-AFM)⁷⁴⁻⁷⁸ are two methods where the second electrode (STM or CT-AFM) tip is physically brought into contact with the molecules assembled on a substrate (See Figure 1.6). Several groups used STM to monitor the electronic properties of alkanethiols, alkylamines, xylyldithiols, phenylene ethynylene oligomers, and conjugated and nitro-substituted self assembled monolayers (SAMs). CT-AFM was used to study the electronic properties of Langmuir-Blodgett films and alkanethiol SAMs. In scanning probe based techniques the measurements are localized to nanometer- or atomic-scale areas. One can select the area and make direct electronic measurements of the molecules supported on a substrate. These techniques can be used to study the electronic properties down to single molecules. SPM based methods are excellent for making several measurements and obtaining statistical data fairly quickly but they do suffer from some disadvantages. With STM, there are questions about the tip-molecule contact. The presence of solvent or the water meniscus can affect the electronic properties observed using STM break junctions.⁷⁹⁻⁸⁰ Factors such as substrate roughness, tip chemistry, extended tip usage, and radius of the tip that is in contact with the monolayer influence the measurements and analysis using AFM. It is also hard to maintain the same tip

Figure.1.6. Schematic representation showing an example where the second electrode is brought into contact with the molecules adsorbed on the surface physically (contacts after). d represents distance and e^- represents electrons.

conditions throughout the experiment. Scanning probe based techniques are not practical as a working device, but are useful for fundamental studies.

1.5.1B2. Electrochemical methods: Electrochemical methods for fabricating metal contacts to molecules have also been reported in the literature. For example, nanowire junctions were previously formed by electrodepositing metal contacts in the pores of polycarbonate membranes (See Figure 1.7A).⁸¹⁻⁸³ Recently, Campbell and coworkers reported an electrochemical method for fabricating metal/molecule/metal junctions.⁸⁴⁻⁸⁵ In their method, they fabricated two electrodes separated by 20 nm by e-beam lithography. They coated one electrode with a SAM and deposited Pt on the second electrode to form a metal/SAM/Pt junction (See Figure 1.7B).

We developed an electrochemical approach for fabricating metal/molecule/metal junctions very similar to Campbell and coworkers. Chapters III, IV, VI and VII discuss the fabrication of metal/polymer/metal or metal/self assembled monolayer (SAM)/metal junctions. Our approach is similar to Campbell and coworkers, except that we use 5 μm gap Au interdigitated array electrodes fabricated by photolithography and form the metal/molecule/metal junctions by deposition of a SAM or polymer at one electrode followed by electrochemical deposition of Ag nanowires (NWs) at the other. The benefit of our approach is the smaller contact area of the junction since Ag NWs serve as one of the electrodes, cheaper and massively parallel fabrication, since we use photolithography, and great versatility in the types of electrodes and molecules that can be placed in the junction.

1.6.The Importance of Sensing Hydrogen:

We describe H_2 sensing applications of E1/nano Pd/E2, E1/nano Pd/polyphenol/E2

Figure 1.7. Schematic representation showing two examples where a second electrode is electrodeposited in order to make a contact with molecules adsorbed on a metal surface (contacts after).

junctions in Chapter III and E1/AgNW/polyphenol/E2 junctions where AgNW is functionalized with Pd nanoparticles in Chapter IV. H₂ sensing is important because H₂ is considered as one of the most useful gases. It is used as a raw material in various industries and also is an intermediary in the manufacturing of synthetic fuels. Scientists even believe that it will soon replace the current fossil-based transportation fuels as an energy source. However, it has a lower explosive limit of 4% in air. Reliable H₂ sensors which could detect H₂ leaks at early stages are required for safety purposes for applications such as fuel cells. Different nanostructures have been highly explored for H₂ sensing. Pd nanostructures are commonly used for H₂ sensing as the reaction between Pd and H₂ is highly selective and well known.

Pd-Hydrogen System: The reaction between Pd and H₂ is well known. When Pd is exposed to H₂ gas, Pd catalyses the reaction where H₂ is dissociated into atomic H. This atomic H adsorbs onto Pd surfaces and diffuses into the Pd lattice to form PdH_x. The reactions are given below:

When H diffuses into the Pd lattice, it undergoes a phase transition from an α -phase to an α - β phase intermediate, and finally to the β -phase at different concentrations or partial pressures of H₂.⁸⁶ This results in an increased Pd-Pd atomic spacing in the material.

When Pd reacts with H₂ and forms PdH_x there is a measurable change in the volume,⁸⁷ optical properties,⁸⁸⁻⁸⁹ and resistance,⁹⁰⁻⁹¹ which can be used as a signal for detecting H₂.

Two types of sensing mechanisms have been demonstrated previously for resistance based H₂ sensors using Pd nanostructures. Type 1 involves well-connected Pd films. In

this case an increase in resistance occurs in the presence of H_2 due to the formation of the more resistive PdH_x material.^{87,92} Type II involves discontinuous Pd thin films or nanostructures containing break junctions. These Pd nanostructures exhibit poor conductivity initially due to the presence of break junctions. In the presence of H_2 , the resistance decreases due to the formation of the PdH_x . This is because formation of PdH_x leads to volume expansion and a more connected structure with fewer high resistance junctions. Figure 1.8 shows a schematic representation of the two types of mechanisms involved in H_2 sensing. Electrode/nano Pd/electrode junctions discussed in Chapter III exhibit the type 1 sensing mechanism, whereas electrode/nano Pd/polyphenol/electrode and electrode/Ag nanowire/polyphenol/electrode junctions where the Ag NW was functionalized with Pd nanoparticles, discussed in Chapter III and Chapter IV exhibit the type II sensing mechanism.

1.7. Surface enhanced Raman spectroscopy (SERS):

History: SERS is a surface sensitive technique that provides a greatly enhanced Raman scattering signal from Raman active molecules that have been adsorbed on rough metal surfaces. In 1974, Martin Fleischman and coworkers observed SERS from pyridine adsorbed on a electrochemically roughened silver electrode.⁹³ They attributed the enhancement to the increased surface area which afforded more binding sites for the pyridine. In 1977, Jeanmaire and Van Duyne⁹⁴ as well as Albrecht and Creighton⁹⁵ independently reported that the enhancement observed by Fleischmann could not be accounted simply to the roughness or the concentration of the scattering species and each proposed a mechanism for the observed enhancement. Jeanmaire and Van Duyne proposed an electromagnetic effect whereas Albrecht and Creighton proposed a charge

A) Type 1

Response

B) Type 2

Figure 1.8. Schematic representation of Type 1 and Type 2 H_2 sensing mechanism.

transfer effect.⁹⁴⁻⁹⁵ SERS has been extensively reviewed by several authors.⁹⁶⁻⁹⁸

Theory: When the electric field [E_0] from a laser is incident on a molecule, the Raman scattering is governed by the relationship

$$E_R = \alpha E_0 \quad (1.3)$$

Where E_R is the Raman scattered signal, α is the molecular polarizability, E_0 is the amplitude of the electric field. From this relationship, it is evident that SERS must involve an increase in one or both of the terms. The two primary theories of “Electromagnetic Model” [EM] and “Charge Transfer Model” [CT] have been proposed as the mechanisms involved in SERS. EM theory addresses an increase in E_0 whereas CT relates to an increase in α . The electromagnetic enhancement is the primary contributor to the observed SERS enhancement as the chemical enhancement provides an 1-2 orders of magnitude enhancement to the Raman signal intensity, while up to 10^{14} enhancements have been reported.⁹⁹

Raman enhancement based on the EM model can be understood with the help of the following derivation and schematic representation shown in Figure 1.9. According to EM theory, there is an increase in intensity of the Raman signal for adsorbates on roughened metal surfaces due to the local electric field enhancement at the surface from surface plasmons and geometric constraints of the metal surface. When the electric field E_0 is incident on the SERS active substrate, localized surface plasmons are excited. Surface plasmons are oscillating electromagnetic fields caused by the conducting electrons in the metal. When the plasmon frequency matches with that of the incoming radiation, the field enhancement is the greatest. The scattered electric field [E_s] is given by:

Figure. 1.9. A) Raman scattering where E_R is the Raman scattered signal and E_0 is the amplitude of the electric field, and B) Surface enhanced Raman scattering of a molecule where E_S is the scattered electric field, E'_R is the Raman scattering signal and E'_{SERS} is the SERS signal.

$$E_s = gE_0 \quad (1.4)$$

where g is the local enhancement factor dictated by the geometric constraints of the metal (roughness factor). This scattered electric field interacts with the molecule to generate the Raman scattering signal, E_R' , which is given by:

$$E_R' = \alpha E_s = \alpha g E_0 \quad (1.5)$$

This Raman scattered field interacts with the metal to produce a SERS signal as is given by

$$E_{SERS}' = g' E_R' = \alpha g g' E_0 \quad (1.6)$$

The intensity of the Raman scattering is proportional to the square of any electromagnetic field incident on the analyte.

$$I_R \propto E^2 \quad (1.7)$$

where I_R is the intensity of the Raman signal and E is the total of the electromagnetic fields. In normal Raman spectroscopy, the signal is very weak as E_a is small in this case. In SERS, the presence of a roughened metal nanostructure in close proximity to the analyte provides an additional electromagnetic field, E_p , providing a large total value of E which results in substantial enhancement of the Raman scattering signal.

$$E = E_a + E_p \quad (1.8)$$

where E_a is the incident electromagnetic field on the analyte in the absence of any roughened metal particles and E_p is the electromagnetic field emitted from the roughened metal particle. In normal Raman spectroscopy, the laser source is far away from the analyte. The signal is very weak as E_a is small in this case. In SERS, the presence of a roughened metal nanostructure in close proximity of the analyte provides an additional

electromagnetic field, E_p , providing a large value of E which results in substantial enhancement of the Raman scattering signal.

Surface Enhanced Raman Spectroscopy (SERS) at hot spots:

SERS has been used to study different molecules adsorbed onto different roughened metal surfaces and nanostructures.⁹⁴⁻⁹⁵ Colloidal Ag or Au particles in the 30-120 nm size range are the most common type of SERS-active substrates. Other examples of SERS active systems include nanoparticle aggregates,¹⁰⁰ rough metal surfaces made by vapor deposition or by electrochemistry,¹⁰¹ island films,¹⁰² and other nanostructures such as ellipsoids,¹⁰³ branched structures, and nanowires with regions of very large curvature.¹⁰⁴⁻¹⁰⁵ An important development in the field was the observation of SERS enhancements of 10^{14} - 10^{15} , which enabled single molecule detection.

Most of the single-molecule SERS studies have focused on the use of metal nanoparticles. In individual nanostructures, the largest E-field enhancement occurs at the particle tips (See figure 1.10A). These fields are further enhanced when two or more particles are placed in close proximity as dimers for example. Brus and coworkers suggested that the narrow junctions between nanoparticles contribute to the giant enhancements which enabled single-molecule detection in SERS active systems.¹⁹ These junctions are termed as hot spots for SERS. Figure 1.10B shows a schematic representation of the hot spots in dimer nanostructures. Electromagnetic fields induced by optical excitation of localized surface plasmon resonance of silver nanoparticles were investigated by Schatz *et al.*¹⁰⁶ Dimers constructed from roughened particles, nanoshells, nanowires, and nanowires decorated with nanoparticles are a few examples of such hot spots.^{104-105,107-111} It has also been reported that nanoscale gap electrodes provide field

A) Individual nanostructures

B) Dimers

Figure 1.10. Schematic representation showing the hot spots in A) Individual nanostructures and B) Dimers.

enhancements large enough for possible single molecule sensitivity.

With a simple geometry of a sharp metallic tip over a planar surface, termed tip enhanced Raman spectroscopy (TERS),¹¹²⁻¹¹³ sufficient field enhancements for single molecule detection have been achieved. Most recently, Li *et al* introduced shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS).¹¹⁴ Here, the surface under investigation is covered with a monolayer of metallic nanoparticles coated with Al or Silica. These nanoparticles play a similar role as that of a tip in TERS. With this approach, several thousands of TERS tips are brought to the surfaces which facilitate rapid probing of the molecular characteristics. In Chapter VI, we describe SERS measurements at electrode/Ag nanowire/ATP/electrode junctions. Our approach is similar to TERS but is on a planar surface. In our devices, Ag nanowires act as the tip in TERS.

1.8. Two Terminal Resistance Switching Devices:

New device concepts and architectures are needed to overcome the physical and economic limitations of current semiconductor devices.¹¹⁵ In this regard, two-terminal resistive switches comprised of molecules or nanostructures, whose conductance can be switched between two states upon application of a voltage are highly pursued as they can be used for ultra high density memory storage or logic devices.¹¹⁶ In general, a resistive switching device structure involves an insulating (organic or inorganic) material that is sandwiched between two electrodes. In some devices whose gapwidth is less than 13 nm resistance switching has been attributed to electromigration at nanogap electrodes. Examples of inorganic materials sandwiched between metal electrodes with resistive switching properties include chalcogenides (Ag-Ge-Se, AgS, and CuS, etc.),¹¹⁷⁻¹¹⁹ metal

oxides (Cu-doped SiO, WO₃, ZrO, and TiO₂, etc.),¹²⁰⁻¹²² and amorphous Si (a-Si).¹²³⁻¹²⁵ Resistive switching in these devices has been explained in terms of the formation of conductive filaments in the insulating layer. The formation of a filament between two electrodes leads to a low resistance state, and its rupture switches the device back to the high resistance state. Figure 1.11 shows a schematic representation of the formation and rupture of a filament upon application of a high voltage. Filament formation could be due to joule heating,¹²⁶⁻¹²⁸ electrochemical processes in binary oxides,¹²⁹⁻¹³⁰ redox processes in ionic conductors such as oxides and chalcogenides,^{128,131} or field-assisted drift/diffusion of ions in TiO or a-Si.¹³²⁻¹³⁵ Amorphous Si based switches exhibited on/off ratios greater than 10³, fast programming speed (5 ns), and long endurance (10⁶ cycles). One drawback is that most of the methods for fabricating these devices use e-beam lithography and are tedious.¹³⁶

Resistive switching has also been observed due to electromigration when high voltages are applied in metal nanogap electrodes whose gap width is less than 13 nm.¹³⁷⁻¹³⁸ These devices are simple in structure as they do not need any material to be sandwiched between the electrodes. They exhibited on/off ratios over 10³, but they require high voltage (10V). One issue is that the fabrication of metal nanogap electrodes often leads to the formation of shorts.

In Chapter VI, we describe a simple electrochemical method to fabricate nanogap electrodes with AgNWs that exhibit reproducible resistive switching behavior. The method described is very simple, highly parallel, has a 100% success rate, does not need any material to be sandwiched between the electrodes, exhibits on/off ratios over 10⁴, and has long endurance (10³ cycles). More importantly, the device requires lower voltage

Figure 1.11. Schematic representation of the formation and rupture of the filament in an electrochemical metallization cell.

(± 2 V) for resistance switching as compared to nanogap electrodes fabricated by other groups.

There are several examples of two terminal molecular switches in the literature. Examples include devices that employ catenanes, rotaxanes, oligophenylene ethylene derivatives, and oligoaniline. The exact mechanism responsible for the conductance switching in these molecules with an applied voltage is still under debate. Several possible mechanisms such as oxidation/reduction of molecules, rotation of molecules, rotation of functional groups, rotation of molecular backbones, interactions with neighbor molecules, fluctuation of bonds, and change of molecule-metal hybridization have been proposed for the observed switching behavior in these molecules. These were based on indirect evidence due to lack of proper characterization tools to determine the structure of the molecules in the junction. In order to better understand the molecular processes responsible for the conductance switching in these systems, spectroscopic techniques such as IETS (inelastic electron tunneling spectroscopy) and SERS are coupled with electrical measurements. In Chapter VII, we describe the fabrication of two-terminal molecular switches using our electrochemical approach with ATP molecules and also an approach to measure conductivity and SERS simultaneously at these junctions.

1.9. Combined SERS and Conductivity measurements:

There are several examples of simultaneous measurements of conductance and SERS at different molecular junctions. This strategy is very powerful for correlating changes in electronic properties with molecular structure in order to elucidate the mechanism of conductance switching.

Hipps and coworkers fabricated Al/AlO_x/phthalocyanine/Pb junctions and reported the Raman spectra of phthalocyanine under two applied biases.¹³⁹ Zou *et al.* reported the Raman spectra at two different potentials for the molecule 1,4 phenylene diisocyanide sandwiched between two gold electrodes.¹⁴⁰ These two groups did not observe any potential-dependent spectral changes, however.

Mc Creery and coworkers fabricated molecular junctions using carbon as a substrate and were the first to report potential dependent spectral changes.¹⁴¹⁻¹⁴² They determined that the TiO_x layer contributed most to the observed conductivity changes in these junctions; the organic layer played a minor role but was necessary to modulate TiO_x conductivity as it acts as a source of electrons.

Natelson and coworkers demonstrated the use of nanoscale gap structures for simultaneous measurements of electronic conduction and Raman spectroscopy of aminothiophenol (ATP).¹⁴³ Crossed nanowire molecular junction arrays were used as a platform for the measurement of current-voltage characteristics simultaneously with IETS and Raman vibrational spectra by Yoon *et al.*¹⁴⁴ Most recently, Tian and coworkers introduced fishing mode tip enhanced Raman spectroscopy to obtain conductance and Raman spectra simultaneously. In Chapter VII, we describe the combination of SERS and electronic measurements at electrochemically-fabricated Ag nanowire/aminothiophenol (ATP)/electrode junctions.

CHAPTER II

EXPERIMENTAL

This chapter includes three parts.

- 1) Techniques used to fabricate and characterize electrode/nanowire/electrode and electrode/nanowire/molecule/electrode junctions
- 2) Substrates and chemicals used in the study.
- 3) Electrochemical procedures for the fabrication of different electrode/nanowire/electrode and electrode/nanowire/molecule/electrode junctions.

2.1. Techniques:

2.1.1. Electrochemistry: All electrochemical measurements were performed using a CH Instruments 660A electrochemical work station using the following techniques:

Cyclic Voltammetry (CV): CV was used to :

- 1) Determine electrochemical deposition potentials for Ag and Pd on Au.
- 2) Electropolymerize phenol on Au.
- 3) Electrochemically desorb aminothiophenol (ATP) from Au.
- 4) Characterize the Au IDA electrode before and after phenol polymerization and aminothiophenol (ATP) desorption.
- 5) Characterize different junctions formed.

All CVs were performed at room temperature with a 5 μm gap Au interdigitated array (IDA) working electrode, Ag/AgCl (3M NaCl) or Ag wire reference electrode, and platinum wire counter electrode. Figure 2.1 shows the setup used to perform all CVs.

Figure 2.1. Digital photograph showing the conventional three electrode setup for metal electrodeposition.

We also obtained CVs in air or i-V curves for measuring the resistance of wires or junctions. For this, we connected the reference and the counter electrode cables to one wire lead of the Au IDA and the working electrode cable to the other lead (see Figure 2.2 for setup). All i-V curves in air were obtained in a Faraday cage.

Chronocoulometry (CC): CC is an electrochemical technique in which the potential of the working electrode is stepped and the number of coulombs passed at the electrode are monitored as a function of time. In our study we used this technique for the controlled deposition of Ag and Pd onto the Au IDA electrodes. The potential of the working electrode was stepped to a potential negative enough to reduce Ag^+ or PdCl_4^{2-} onto the Au IDA.

Chronoamperometry (CA): CA is an electrochemical technique where one steps the potential of the working electrode and monitors the current as a function of time. We used this for H_2 sensing, resistance switching, and combined SERS and conductivity studies.

Linear Sweep Voltammetry (LSV): LSV was used to strip the Ag nanowires to fabricate two terminal resistive switches in Chapter V.

2.1.2. Scanning Electron Microscopy: Scanning electron microscopy (SEM) images were obtained with a FEI-NOVA-600 NANO SEM. SEM was used to image all the devices fabricated in the study to get information about the size and shape of the wires and also determine the number of connections or wires on a device.

2.1.3. Surface Enhanced Raman Spectroscopy (SERS): SERS was used to determine the enhancement factor of a Raman signal for molecules sandwiched between Au and Ag electrodes, versus molecules adsorbed on the surface and edges of the Au IDA electrode.

Figure 2.2. Digital photograph showing the two electrode setup for i-V measurements in air in CV mode of the CHI660A.

The intensity of the Raman signal was measured for aminothiophenol (ATP) adsorbed on Au through Au-thiol bonding. The spectra were excited with 5 mW of 632.8 nm radiation from a HeNe laser using a Renishaw micro Raman system in the 1000-1800 cm^{-1} range.

2.1.4. Atomic Force Microscopy: Atomic force microscopy (AFM) images were obtained with a Veeco Digital Instruments Nanoscope IIIa Multimode scanning probe microscope using a Si nitride tip in contact mode. AFM was used to measure the thickness of the polyphenol film electrodeposited onto the Au IDA electrodes.

2.1.5. Simultaneous conductivity and SERS measurements: The Au electrode was stepped to different potentials and the current vs time and the SERS spectra were measured simultaneously. Simultaneous conductivity and SERS measurements were obtained in order to correlate the electronic properties of junctions containing ATP with the structural properties. Figure 2.3 shows a schematic representation of the setup used for obtaining conductivity and SERS measurements at metal/molecule/metal junctions simultaneously.

2.2. Substrates and chemicals.

2.2.1. Microfabrication of Au Electrodes on Si/SiO_x. 5 μm gap Au interdigitated array (IDA) of electrodes were used as substrates for depositing different metals, polymers, and molecules to fabricate metal and molecule based electronic devices for sensing, surface enhanced Raman spectroscopy (SERS), and molecular electronics applications. Figure 2.4 shows digital and SEM images of the Au IDA. The Au IDA electrodes were microfabricated in a cleanroom using photolithography, sputtering, and liftoff processes. A detailed description of these steps is given below.

Figure 2.3. Schematic representation of the setup used to obtain simultaneous conductivity and SERS measurements at metal/molecule/metal junctions.

Figure 2.4. A) Digital photograph and B) SEM image of square region from frame A of an Au IDA electrode.

Photolithography. Photolithography allows one to form the patterned Au IDA electrodes on Si/SiO_x substrates. First a SiO_x layer was formed on Si by heating the Si wafer in a furnace at 1100 °C by a procedure known as thermal oxide growth. Second, hexamethyldisilazane (HMDS) was spin coated (Solitech Spinner, Model 5100) on the Si/SiO_x wafer by placing a few drops of HMDS onto the wafer mounted on a vacuum chuck following the standard parameters: a) 500 revolution per minute (rpm) for 0.2 s, b) 4000 rpm for 10 s, and c) 4000 rpm for 9.9 s. Third, positive resist “1823” was spin coated using the standard spin coating parameters. Positive resist is relatively insoluble in the developer until exposed to light at which point the exposed portion exhibits increased developer solubility. In simple terms, whatever is exposed to light goes away. A negative resist is relatively soluble in the developer until exposed to light, at which point the exposed portion exhibits decreased developer solubility. Figure 2.5 illustrates negative and positive photoresist behavior. After coating the wafer uniformly with HMDS and 1823, the wafer was placed on a hot plate at 115 °C for 1.5 min (soft bake) to drive off solvents, improve adhesion, and anneal away the stress introduced during the spin process. Next, a Karl Suss Mask Aligner MA6/BA6 was used to align the mask with the wafer to transfer the pattern from the mask to the wafer. The mask has the pattern of the Au IDA. The mask and wafer were aligned and placed in close proximity (~125 μm) in the aligner. The photoresist was exposed through the pattern of the mask with a high intensity UV-light for ~5.5 s. The wafer was then immersed in MF-319 developer (95% water, <1% surfactant, and 2.2% tetramethylammonium hydroxide) for ~1 min followed by rinsing with DI water and drying under a N₂ gun. The areas of photoresist exposed to UV-light were washed away as the exposure of 1823 to UV light leads to a chemical

Figure 2.5. A) Negative photoresist and B) Positive photoresist. E represents region exposed to UV radiation and UE represents area not exposed to UV radiation.

structural change in the polymer, making it more soluble in the developer. Finally, a hard bake at same temperature as soft bake (115°C) for 2.5 min was performed to harden the photoresist and improve adhesion to the wafer.

Sputtering. Sputtering is a process where a solid target material is bombarded with energetic particles (ions), which results in the ejection of the atoms from the solid target. These ejected atoms are then deposited on top of the photoresist patterned wafer. An argon (Ar^+) ion source was used to sputter Cr, Ti or Ni targets as adhesion layers, followed by Au to form Au IDA electrodes. The thickness of the adhesion layer was 10 Å and the Au layer was 100 nm. The sputtering was carried out using a Techincs RF/DC Sputterer, Model 4604 under high vacuum conditions ($\sim 5 \times 10^{-10}$ torr).

Lift off. The photoresist and parts of Au sputtered on top of the photoresist were removed by immersing the Au –coated wafer in an acetone shaking bath for a few hours. Au, Cr or Ti particles that were not removed by sonication were removed using a Q-tip. Removal of the photoresist and metal on top of it leaves the patterned Au IDA electrodes remaining on the Si/SiO_x . This is known as lift-off. Finally, the wafer was diced in a disco dicing saw (Hi-Tech America Inc., DAD321) to separate the individual electrode devices for further use.

2.2.2. Wiring and Cleaning of the Au IDA Electrodes: Figure 2.6 shows the steps involved in preparing the Au IDA electrode for electrochemical and electronic studies. First, the wires were attached to the electrode contact pads with Ag epoxy (Stan Rubinstein Assoc. Inc., Foxboro MA) and placed in an oven for ~12h at 80°C in order to cure the epoxy. The wires were further insulated with an overlayer of torr-seal epoxy and cured ~12 h at 80°C. The electrode was then cleaned by rinsing in acetone, ethanol, 2-

Figure 2.6. Steps involved in wiring and cleaning the electrode devices.

propanol, nanopure water and drying under N₂. The electrode was placed in a UV ozone cleaner (Jelight Company Inc., Irvine, CA, Model 4C442) for 15 min in order to remove organic impurities. Electrodes were also cleaned electrochemically by cycling several times from 0 to 1.2 V at 100 mV/s in 0.1 M H₂SO₄ until we observed a well-pronounced oxidation and reduction peak for Au. Figure 2.7 shows a cyclic voltammogram of an Au IDA electrode in 0.1M H₂SO₄. The peaks at ~1.0 V and ~0.6 V represent the Au oxidation and reduction peak respectively.

2.2.3. Chemicals. Silver nitrate (99%), Potassium tetrachloropalladate (98%), potassium hydroxide pellets, 85+%, A.C.S. reagent, 4-aminothiophenol, tech., (90%), Phenol, (99+%), butanethiol (99%), hexanethiol (95%), dodecanethiol (98%), octadecanethiol (98%) and octanedithiol(99%) were purchased from Sigma-Aldrich. Potassium ferricyanide was purchased from Merck. Potassium perchlorate was purchased from Parr instrument company. Sulfuric acid was purchased from VWR. Barnstead Nanopure water (17.8 MΩ-cm) was employed for all aqueous solutions.

2.3. Electrochemical Procedures. After preparing, wiring and cleaning the Au IDA electrodes, several different electrochemical procedures were used to prepare electrode/nanowire/electrode and electrode/nanowire/molecule/electrode junctions. The procedures are described in the next sections. Metal (Ag and Pd) electrodeposition, electropolymerization of phenol, and self assembled monolayer desorption were performed using a conventional three electrode set up.

2.3.1. Electrodeposition of Pd nanostructures across the microgap electrodes. In order to grow Pd nanostructures across the microgap electrodes, first the deposition potential and the number of coulombs of Pd to be electrodeposited to make connection

Figure 2.7. i-V curve of bare Au IDA in 0.1M H_2SO_4 vs Ag/AgCl reference electrode. Scan rate was 100 mV/s.

between electrodes were determined.

Determination of Deposition Potential: The potential for Pd electrodeposition was determined by obtaining a cyclic voltammogram of Au IDA in 5mM PdCl_4^{2-} in 0.1M H_2SO_4 at a scan rate of 100 mV/s using an Ag/AgCl reference electrode and Pt wire counter electrode. Figure 2.8A shows a CV of the Au IDA in 5mM K_2PdCl_4 in 0.1M H_2SO_4 . Pd was in the oxidized form in the solution thus, the potential was scanned in the negative direction starting from a potential where no reduction occurs (in this case 0.8 V). As the potential approaches the characteristic E^0 (~0.2 V) for the redox process, a cathodic current begins to flow, until a peak is reached. The direction of the potential sweep was reversed after traversing the potential region in which the reduction process takes place. The peaks at ~0.2 V and ~0.45 V represent the cathodic (Pd^{2+} to Pd^0) and anodic (Pd^0 to Pd^{2+}) peaks. The dashed line (-0.1V) in the Figure 2.8A represents the potential at which Pd electrodeposition was performed to grow nanostructures across the micron gap electrodes. Based on the CV, the rate of deposition was diffusion controlled at this potential (-0.1 V). Chronocoulometric mode was used to deposit nanostructures in a controllable manner.

Determination of charge: First, the background current of the Au IDA device was obtained in air, and usually the background current of the Au IDA device was around 8.0×10^{-11} A at 1V. Later, different numbers of coulombs of Pd were electrodeposited across the electrodes, and then an i-V curve was again obtained in air. Figure 2.8B shows the chronocoulometric plot of an Au IDA electrode in 5mM K_2PdCl_4 at -0.1V. Fig 2.8C shows a plot of the different number of coulombs of Pd electrodeposited on E1 vs the solid-state device current. We observed that the currents were in the milliamp range at

Figure 2.8. (A) Cyclic voltammogram of Au IDA electrode in 5 mM K_2PdCl_4 plus 0.1M H_2SO_4 at a scan rate of 100 mV/s. The dashed line represents the potential at which Pd was electrodeposited in order to grow Pd nanostructures across the Au IDA. (B) Chronocoulometric plot of Au IDA electrodes in 5mM K_2PdCl_4 at -0.1V and (C) Charge vs solid state current plot showing number of coulombs of Pd required to make connections between the electrodes. Ag/AgCl was used as a reference electrode and a Pt wire as the counter electrode.

at 1 V when 1.2×10^{-4} or more coulombs of Pd was electrodeposited indicating that the two electrodes were connected. Hence, to grow Pd nanostructures across the microgap electrodes, a total of 1.2×10^{-4} Coulombs of Pd was electrodeposited on one set of electrodes (E1) from a solution containing 5 mM PdCl_4^{2-} in aqueous 0.1 M H_2SO_4 at -0.1 V using an Ag/AgCl as reference electrode and Pt wire counter electrode. Pd was electrodeposited only on one set of electrodes (E1) by connecting one wire lead of the IDA to the potentiostat as the working electrode.

2.3.2. Fabrication of a H_2 Switch. Fabrication of a “ H_2 Switch” involves electropolymerization of phenol on one set of electrodes (Electrode 2, E2) by cycling from 0.0 to 1.2V at 100mV/s in a 5 mM phenol solution in 0.1M H_2SO_4 for 4 to 10 cycles. Figure 2.9A shows the CV of an Au IDA electrode in 5mM phenol in 0.1 M aqueous H_2SO_4 . The anodic peak at ~ 1.0 V represents the phenol oxidation. We observed a decrease in peak current of phenol oxidation with subsequent scans, indicating the formation of a resistive polyphenol film. The formation of polyphenol film on the electrode was confirmed by observing the electrochemistry of a 0.05 M $\text{Fe}(\text{CN})_6^{3-}$ in KClO_4 solution before and after polyphenol film formation. Figure 2.9B shows the cyclic voltammograms of an Au IDA electrode in 0.05 M $\text{Fe}(\text{CN})_6^{3-}$ in KClO_4 before and after electropolymerization of phenol on the Au electrode. Before electropolymerization (on the bare Au IDA electrode), we observed $\text{Fe}(\text{CN})_6^{3-}$ reduction and $\text{Fe}(\text{CN})_6^{4-}$ oxidation peaks centered near 100mV. After polymerization, we did not observe the reduction and oxidation peaks because the polyphenol film hinders electron transfer from the electrode to the $\text{Fe}(\text{CN})_6^{3-/4-}$ ions present in solution. After confirming the polyphenol film formation on electrode 2 (E2), Pd was electrodeposited on E1 as described in

Figure 2.9. i-V curves A) of bare Au IDA in 5 mM phenol in 0.1 M H₂SO₄ (10 cycles) and (B) Au IDA in 0.05 M Fe(CN)₆³⁻ solution before and after polyphenol film formation. Scan rate was 100 mV/s and potentials reported vs Ag/AgCl reference electrode in all cases.

section 2.3.1.

2.3.3. Electrodeposition of Ag nanowires (NWs). First, a cyclic voltammogram of an Au IDA electrode in 5 mM AgNO₃ in aqueous 0.1 M H₂SO₄ using an Ag wire quasi reference electrode and Pt wire counter electrode at a scan rate of 100 mV/s was obtained to determine the potential at which Ag electrodeposition occurred to grow Ag NWs across the micron gap electrodes. Figure 2.10A shows the cyclic voltammogram of an Au IDA in 5 mM AgNO₃ in aqueous 0.1 M H₂SO₄. The peaks at ~0.0 and ~0.05 V represent Ag reduction and oxidation respectively. The dashed line (-0.3 V) indicates the potential used to electrodeposit Ag NWs. Figure 2.10B shows the chronocoulometric plot of an Au IDA electrode in 5 mM AgNO₃ at -0.3V. Figure 2.10C shows a plot of the number of coulombs of Ag deposited on E1 vs solid state device current. The current was in the milliamp range at 1V once 6.0×10^{-5} or more coulombs of Ag was electrodeposited. Hence, Ag NWs were grown on one set of electrodes (E1) by electrodeposition of 6.0×10^{-5} Coulombs of Ag (t ~12 s) from a solution containing 5 mM AgNO₃ in aqueous 0.1 M H₂SO₄ at -0.3 V using an Ag wire quasi reference electrode and Pt wire counter electrode. The deposition was performed in chronocoulometry mode by connecting one wire lead of the IDA to the potentiostat as the working electrode.

2.3.4. Fabrication of E1/Ag NW/polyphenol/E2 junction. E1/Ag NW/polyphenol/E2 junctions were prepared on Au IDA electrodes, where E1 and E2 represent the two sets of IDA fingers. Phenol was electropolymerized on E2 by cycling the potential (3-10 cycles) from 0 to 1.2 V at 100 mV/s in a 5 mM phenol solution in 0.1 M H₂SO₄ with an Ag/AgCl reference electrode and Pt counter electrode. The formation of a polyphenol film on the electrode was confirmed by observing the electrochemistry of a 0.05 M Fe(CN)₆³⁻

Figure 2.10. (A) Cyclic voltammogram of Au IDA electrode in 5 mM AgNO_3 plus 0.1M H_2SO_4 at a scan rate of 100 mV/s. The dashed line represents the potential at which Ag was electrodeposited in order to grow Ag nanowires across the Au IDA. (B) Chronocoulometric plot of Au IDA electrodes in 5mM AgNO_3 at -0.3V and (C) Charge vs solid state current plot showing the number of coulombs of Ag required to make connections between the electrodes. An Ag wire was used as a reference electrode and Pt wire as the counter electrode.

solution before and after polyphenol film formation. Later, Ag was electrodeposited on E1 as described in section 2.3.3.

2.3.5. Synthesis of Pd Monolayer-Protected Clusters (MPCs). Octylamine coated Pd clusters were synthesized as described previously.¹⁴⁵ Briefly 0.5 g of K_2PdCl_4 was dissolved in 20 mL of nanopure water to prepare a 1.59 mM aqueous K_2PdCl_4 solution. Next 1.92, g of tetraoctylammonium bromide (TOABr) was added to 100 mL of toluene (3.51 mM) and sonicated for 10 min in order to ensure complete dissolution. The aqueous K_2PdCl_4 solution was then added to the toluene TOABr solution and stirred for 10 to 20 min until all of the Pd salt transferred into the toluene phase as $\text{PdCl}_4^{2-}(\text{TDA})_2^+$ or $\text{PdCl}_4^{2-}(\text{TOA}^+)(\text{K}^+)$. The orange aqueous layer turned colorless and the colorless toluene layer turned red, indicating the transfer of the PdCl_4^{2-} . The ratio between K_2PdCl_4 and TOABr was 1:1.2. The toluene phase was separated using a separatory funnel and then 3.10 mL of octylamine was added and the solution stirred for 2 h. The molar ratio of alkylamine to Pd was 12:1. Due to the formation of a complex between the protonated octylamine and PdCl_4^{2-} , the solution turned a beige murky white color immediately after the addition of octylamine. 0.84 g of NaBH_4 was then dissolved in 10 mL of water and added to the two phase solution while stirring. The solution turned black after a few seconds indicating the formation of Pd MPCs. An additional 10 mL of water was added to the solution and the solution stirred overnight. The water phase turned clear as the reaction proceeded. The toluene layer was separated and removed by rotary evaporation. The remaining black solid was suspended in acetonitrile and filtered through a glass-fritted Buchner funnel. The collected black solid product was further

cleaned by washing it with 150 mL of acetonitrile and 150 mL of ethanol over the Buchner funnel. The product was dried thoroughly before use.

2.3.6. Functionalization of Ag NWs with Pd MPCs for H₂ Sensing. E1/Ag

NW/polyphenol/E2 junctions were fabricated following the procedure described under section 2.3.4. Devices which had 10 cycles of polyphenol on E2 and Ag on E1 were placed in a solution containing 2 mM 1,8-octanedithiol in ethanol for 1 h, rinsed with ethanol, and finally dried under N₂. The device was then placed in a toluene solution containing 8.2 mg/mL octylamine-coated Pd monolayer-protected clusters, synthesized as described previously, for 20 min, followed by rinsing in toluene and IPA and finally drying under N₂. Octanedithiol chemisorbs strongly to the Ag nanowires and Au electrodes (E2 and E1). The Pd MPCs attach to the free thiolate group of octanedithiol.

2.3.7. H₂ Sensing Set-Up. Figure 2.11 shows the setup used for H₂ sensing. H₂ gas sensing experiments were performed with an electrochemical work station (CH Instruments, Inc., Model 660A) operating in chronoamperometry (CA) mode which plots current vs time. The current was monitored with time while a constant -0.3 V potential was applied between the two electrodes. Samples were exposed to alternating flows of pure N₂ and different concentrations of H₂ in the N₂ carrier gas. The equation for calculating the percent of H₂ in the environment is described below:

$$FM_4 \text{ (mL.min}^{-1}\text{)} / \{FM_1 \text{ (mL.min}^{-1}\text{)} + FM_4 \text{ (mL.min}^{-1}\text{)}\} \times 100 = \% \text{ H}_2 \quad (2.1)$$

FM₄ denotes the variable flow of hydrogen (mL.min⁻¹) in flow meter #4 and FM₁ corresponds to the constant flow of nitrogen through flow meter #1. A sample calculation is shown in Table 2.1.

Figure 2.11. Schematic representation of H₂ sensing set-up.

Table 2.1 Sample calculation for % H₂.

Nitrogen Flow meter 1 Scale reading 150	Hydrogen Flow meter 4 Scale reading 80	Total flow FM1+FM4	Percent Hydrogen (FM4/Total flow)×100
2826ml/min	300ml/min	3126ml/min	9.6%

2.3.8. Fabrication of SAM based devices (E1/Ag NW/SAM/E2 junctions). E1/Ag NW/self assembled monolayer (SAM)/E2 junctions were prepared on the Au IDA electrodes, where E1 and E2 represent the two sets of IDA fingers. First the SAM of interest was assembled on both sets of electrodes by placing the device in a 2 mM ethanol solution of an alkanethiol (hexanethiol, dodecanethiol, octadecanethiol or aminothiophenol) for 12 to 15 h. Formation of a SAM on E2 was confirmed by observing the electrochemistry of 0.05 M $\text{Fe}(\text{CN})_6^{3-}$ in KClO_4 (See Figure 2.12). The SAM was then electrochemically desorbed from one set of electrodes (E1) by sweeping the potential from -0.2 to -1.2 V five times in 0.1 M KOH in ethanol solution using an Ag/AgCl reference electrode and Pt counter electrode.¹⁴⁶ Desorption of the SAM was confirmed by observing the electrochemistry of 0.05 M $\text{Fe}(\text{CN})_6^{3-}$ in KClO_4 (see Figure 2.12). Finally, Ag was electrochemically deposited on E1 as described previously in section 2.3.3.

2.3.9. Fabrication of Resistance Switching Devices. Ag NWs were grown on one set of electrodes (E1) as described previously under section 2.3.3. Ag was later stripped from E2 by scanning the potential from -0.1 to 0.6 V in 0.1 M H_2SO_4 at a scan rate of 100 mV/s using an Ag/AgCl reference electrode and Pt counter electrode. The sample was then rinsed with nanopure water and dried under nitrogen. A current-time plot was then obtained in air. If the current obtained at 1 V was higher than the background current (before electrodeposition of Ag), Ag was stripped from E2 again. This was repeated (1-2 times) until the current at 1 V dropped to the original background current.

2.3.10. Metal filament formation through the monolayer in E1/AgNW/ATP/E2 junctions. E1/AgNW/ATP/E2 junctions were fabricated as described in section 2.3.8. In

Figure 2.12. i-V curves in 0.05 M $\text{Fe}(\text{CN})_6^{3-}$ solution of Bare Au IDA (Blue), Au IDA coated with ATP (Black) and after removing (desorption) ATP from the Au IDA (Red). The scan rate was 100 mV/s. Potential reported vs Ag/AgCl reference electrode.

this case, 1.0×10^{-5} C of Ag was electrodeposited onto E1 to purposefully make a short circuit through the ATP SAM as confirmed by a current-voltage plot. Later, Ag was stripped from E2 in 0.1 M H_2SO_4 by scanning the potential from -0.1 to 0.6V in 0.1M H_2SO_4 at a scan rate of 100 mV/s using Ag/AgCl as a reference electrode and Pt as a counter electrode. The sample was then rinsed with nanopure water and dried under nitrogen. A current-time plot was obtained in air. If the current obtained at 1 V was higher than the background current before Ag electrodeposition, Ag was stripped from E2 again. This was repeated (1-2 times) until the current at 1 V dropped to the background level.

CHAPTER III

HYDROGEN SWITCHES AND SENSORS FABRICATED BY COMBINING ELECTROPOLYMERIZATION AND PALLADIUM ELECTRODEPOSITION AT MICROGAP ELECTRODES

¹Here we describe a simple electrochemical approach to fabricate devices which behave as hydrogen sensors and switches. Devices fabricated by the electrodeposition of Pd directly across a 5 micron-gap interdigitated array (IDA) of gold electrodes behaved as “hydrogen sensors”. These devices had initial currents on the 10^{-3} A level at -0.3 V and exhibited fast and reversible decreases in current in the presence of H₂ concentrations in a N₂ carrier gas with an average detection limit of 400 ppm. The current decrease is due to the formation of more resistive PdH_x in the presence of H₂. Devices fabricated by polyphenol electropolymerization on one set of electrodes and Pd electrodeposition on other set behaved as “H₂ switches”. These devices displayed very low baseline currents of 10-100 pA at -0.3V due to the presence of polyphenol in the Electrode1/Pd/Polyphenol/Electrode 2 junction and the current increased a remarkable 7-8 orders of magnitude in the presence of >1% of H₂ due to volume expansion upon PdH_x formation, which leads to a direct connection between Pd as (PdH_x) and Electrode 2 through the porous 4-10 nm thick polyphenol insulating film. The response and recovery time for the “hydrogen sensor” ranged from 20-60 s while that for the “hydrogen switch” ranged from 10 to > 100 s. The response and recovery time generally decreased for the

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“hydrogen switch” as the number of polyphenol electrochemical cycles decreased.

3.1. INTRODUCTION

Here we describe a simple, highly reproducible electrochemical method for fabricating Pd-based H₂ sensors and switches. This work was inspired by Penner and co-workers,^{45,91} who electrochemically-synthesized an array of Pd mesowires on the step-edges of highly-oriented pyrolytic graphite and studied their resistance change in the presence of H₂. They observed a significant decrease in resistance due to the connection of break junctions within the mesowires upon volume expansion of PdH_x.^{45,91} This mechanism led to devices with larger and faster responses compared to traditional Pd-based H₂ sensing devices.^{87,92} Our group and others reported H₂ sensing with films of Pd nanoparticles^{145,147-149} containing nanoscale gaps that operate on similar principles.

The approach described here importantly leads to Pd/electrode junctions with controlled responses to H₂ by uniquely combining Pd electrodeposition and phenol electropolymerization at microgap electrodes with the benefits of 1) a direct contact formed between the Pd structures and the electrodes during synthesis, eliminating the need for multistep processes involving transfer, assembly, lithography, and contact formation common in electronic-based micro-/nano-sensing devices that lead to long fabrication times and device failures, 2) a simple, fast, highly parallel process with a 100% success rate, and 3) general applicability for fabricating a wide range of metal/organic/metal junctions.

3.2. EXPERIMENTAL

Figure 3.1 illustrates the two methods used to electrochemically fabricate devices on Au interdigitated array (IDA) electrodes (10 or 14 fingers) separated by a 5 μm gap.

Figure 3.1. Schematic representation of methods for forming H₂ sensors and switches.

Procedure A, referred to as a “H₂ Sensor”, involves electrodeposition of 2.4×10^{-4} coulombs of Pd on one set of electrodes (Electrode 1, E1) from a 5 mM PdCl₄²⁻ solution at -0.1 V vs. Ag/AgCl. Procedure B, referred to as a “H₂ switch”, involves electropolymerization of phenol on one set of electrodes (Electrode 2, E2) by cycling from 0.0 to 1.2 V at 100 mV/s in a 5 mM phenol solution in 0.1 M H₂SO₄ for 4 to 10 cycles followed by the same Pd electrodeposition procedure on E1 used in Procedure A. Refer to Chapter 2 for the details.

3.3. RESULTS AND DISCUSSION

Figure 3.2, Frames A and B, shows scanning electron microscopy (SEM) images of the entire array of 10-finger IDA electrode devices containing a E1/Pd/E2 and a E1/Pd/polyphenol (10 cycles)/E2 junction of a “H₂ sensor” and “H₂ switch”, respectively. Frames C and D, shows expanded SEM images of circled portions in Frame A (H₂ sensor) and B (H₂ switch) respectively. Pd electrodeposited on E1 crossed over to E2 with a dendritic or flower-like structure. Figure 3.3, Frames A and B, shows the corresponding current-voltage plots for “H₂ sensor” and “H₂ switch” respectively. The “H₂ sensor” is ohmic, exhibiting a current of 13.0 mA at -1.0 V ($R = 77\Omega$). The “H₂ switch” exhibits a current of 2.09 nA at -1.0 V ($R = 478\text{ M}\Omega$), but there is significant hysteresis in the plot. Current-time plots of a H₂ sensor and switch (Frames C and D in figure 3.3) show that the current is constant in the mA range with time for the former, but exponentially decays by 1 to 2 orders of magnitude down to the 10 to 100 pA range with time for the latter (close to the device background). The high resistance of the “H₂ switch” is due to the low electronic conductivity of the polyphenol film between E2 “H₂ switch” is due to the low electronic conductivity of the polyphenol film between E2

Figure 3.2. SEM images of (A) The entire array of 10-finger IDA electrode device containing a E1/Pd/E2 junction (H₂ sensor) (B) The entire array of 10-finger IDA electrode device containing a E1/Pd/polyphenol (10 cycles)/E2 junctions of a (H₂ switch) (C) Zoomed in image of the circled portion of frame A (H₂ sensor) and (D) Zoomed in image of the circled portion of frame B (H₂ switch).

Figure 3.3. (A) i-V curve of H₂ sensor (B) i-V curve of H₂ switch (C) Current-time plot of H₂ sensor (different device from the one showed in figure 3.2) and (D) Current-time plot of H₂ switch. Current-time plots are obtained at -0.3 V. The H₂ sensor maintains a constant current in the mA range with time, consistent with electronic conduction through the Pd at the E1/Pd/E2 junction. The current through the H₂ switch drops from the 10⁻¹⁰ A level to the low 10⁻¹¹ A level (~10 pA), consistent with stray ionic conductance or capacitive charging of the E1/Pd/Polyphenol/E2 junction and practically no electronic conductance through the polyphenol film, as expected.

and the Pd (Figure 3.1B) while the hysteresis and exponentially decaying current-time plot reveals some stray ionic conductance within the film.¹⁵⁰ Based on the known conductivity of Pd ($94,800 \Omega^{-1}\text{cm}^{-1}$), the current observed for the “H₂ sensor” device corresponds to a contact area of only 83 nm x 83 nm. This value is much smaller than the apparent contact area observed from the top view SEM images. Table 3.1 provides information about the device current, resistance, number of apparent connections from top view, and contact area based on the resistance for the devices studied. The number of apparent connections varied while the device current was within one order of magnitude for at least three samples of each type of device. These differences did not qualitatively affect the highly reproducible response to H₂. Side-view SEM images of “H₂ switch” devices in Figure 3.4 reveal that the Pd deposits vertically and horizontally from E1 preferentially at the edges of the electrodes and apparent connections viewed from the top as in Figure 3.2 may not actually be in contact with E2. For example Frame D in figure 3.4 shows a side view image of a Pd wire that is not in contact with E2 where as from the top view it looks connected. Also it is evident from the side view images that though Pd starts depositing in dendritic or flower like fashion from E2 the actual Pd that is contact with E2 is smaller (See frame F in figure 3.4). This and possible high contact resistance likely explains the small contact area calculation.

Figure 3.5, shows the current at -0.3 V as a function of time for a 10-finger IDA “H₂ sensor” in the presence of 100% N₂ (H₂ “off”,) and various H₂ concentrations (H₂ “on”,) as indicated. The current was initially stable in N₂ and then decreased reversibly in the presence of H₂ due to the formation of PdH_x, which is more resistive compared to Pd. The non-linear response between 1.0% and 3.1% H₂ is due to the well-known α -

Table 3.1. Number of connections, current, resistance, and contact area for H₂ sensor and switch devices

H₂ Sensor					
sample	# of fingers in IDA	# of apparent connections (top view)	Current at -1V from i-V curve (A)	Resistance at -1V(Ω)	Contact Area
1*#†	10	6	1.30×10^{-2}	76.9	83×83 nm
2	10	1	1.37×10^{-2}	73.0	85×85 nm
3	10	5	8.29×10^{-3}	122	66×66 nm
H2 Switch-10 cycles Phenol					
sample	# of fingers in IDA	# of apparent connections (top view)	Current at -1V from i-V curve (A)	Baseline current from current-time plots (pA)	
1	14	19	8.25×10^{-8}	10-100	
2†	10	3	1.30×10^{-8}	10-100	
3‡	14	24	8.60×10^{-9}	10-100	
4	---	----	1.30×10^{-8}	10-100	
5*#‡	10	4	2.09×10^{-9}	10-100	

* SEM images of these samples are shown in Figure 3.2.

current-voltage plots of these samples are shown in Figure 3.3.

† current-time sensing plots of these samples are shown in Figure 3.5.

‡ current-time sensing plots of these samples are shown in Figure 3.9.

Figure 3.4. SEM images of H_2 switches (10 cycles phenol). (A) Side view of entire IDA and (B) Expanded image of a Pd structure (side view). (C) Top view of a single Pd structure as compared to a (D) Side view of a structure showing more details of the junction. (E) A side-view of another H_2 switch and an (F) Expanded image of the region highlighted by the dashed box. These images overall show that the Pd grows upward and outward from the Au IDA electrodes. Apparent connections viewed from the top view SEM images may not actually be in contact with Electrode 2. Although the images do not conclusively show the polyphenol, we believe the polyphenol prevents intimate contact between Pd and Electrode 2, leading to the high resistance of these devices in the absence of H_2 . In the presence of $>1.0\%$ H_2 , the Pd expands in volume as PdH_x through the polyphenol film to make direct contact with Electrode 2.

Figure 3.5. Current-time plot of H₂ sensor device measured at -0.3V in the presence of N₂ initially and in the presence of various concentrations of H₂ (H₂ on) and 100% N₂ (H₂ off) as indicated.

to β -phase-transition that occurs during PdH_x formation^{87,151} and above 3.1% the sensor approaches H saturation. Calibration curves from 0.0 to 0.78% H_2 (Figure 3.6) for three devices reveal an average slope and theoretical limit of detection of 0.58 ± 0.11 and $0.04 \pm 0.03\%$ H_2 , respectively (Table 3.2). The average response and recovery time ranges from 20 to 60 s (Table 3.3). Note that the 3% change in the Pd resistance for our H_2 sensor at 9.6% is smaller than the $\sim 20\%$ change previously reported by Sakamoto *et al.* We believe the resistance increase of PdH_x is counteracted by a resistance decrease caused by an increase in contact area upon volume expansion of PdH_x . This leads to a smaller increase in resistance than expected (See Figure 3.7).

Figure 3.8, Frame A, shows the dramatically different behavior of the “ H_2 switch”, which displays a remarkable increase in current by 7-8 orders of magnitude above 1.0% H_2 (see Figure 3.8B for 1.0% H_2). For example, at 3.1% the current increased from about 1.0×10^{-11} A to 1.1×10^{-3} A. We believe the large increase in current is due to the volume expansion of PdH_x through the 4-10 nm thick polyphenol layer (Figure 3.9), leading to direct contact with E2 (See Figure 3.10 for the schematic representation of the mechanism involved in the H_2 Switch. This likely occurs through pores present in the polyphenol film. Figure 3.9 shows the porous nature of the polyphenol film electrodeposited on Au IDA. The thickness of the polyphenol film was obtained by contact mode atomic force microscopy (AFM). For this, 10 cycles of polyphenol was electrodeposited on an Au IDA. Later, a portion of it was scratched away with an AFM tip. The thickness of the polyphenol film was determined by measuring the height of the scratched area. This proposed mechanism, which is similar to that described by Penner and co-workers for Pd mesowires containing nanoscale break

Figure 3.6. Graphs of percent response vs H₂ concentration for all H₂ sensor devices over (A) The entire range of 0.11 to 9.6% H₂ and (B) The linear range of 0.11-0.78% H₂. The percent response is defined as $(i_r - i_b)/i_b \times 100\%$, where i_r is the current in the presence of H₂ and i_b is the baseline current in the presence of N₂ before exposure to H₂.

Table 3.2. Percent responses for three different H ₂ sensor devices as a function of H ₂ concentration along with the linear slope and limit of detection for each device.					
Sample	1	2	3		
% H₂	% response	% response	% response	AVG	STD
9.6	2.61±0.01	2.74±0.02	2.77±0.06	2.71	0.09
6.0	2.12±0.12	2.69±0.01	2.64±0.04	2.48	0.32
3.1	1.93±0.23	2.48±0.01	2.22±0.01	2.21	0.27
1.0	0.76±0.02	0.80±0.02	0.96±0.01	0.84	0.11
0.78	0.37±0.02	0.44±0.14	0.52±0.02	0.44	0.08
0.48	0.24±0.01	0.25±0.01	0.37±0.01	0.28	0.07
0.21	0.10±0.01	0.13±0.01	0.17±0.02	0.13	0.04
0.11	0.04±0.02	0.04±0.01	0.06±0.01	0.05	0.01
Sample	1	2	3		
Linear slope (% res./%H₂)	0.48	0.56	0.69	0.58	0.11
Limit of detection (%H₂)	0.06	0.05	0.01	0.04	0.03

Table 3.3. Response and recovery times for three different H₂ sensor devices as a function of H₂ concentration.

H₂ Sensor	Response time				
% H₂	sample 1	sample 2	sample 3	AVG	STD
9.6	17	29	24	23	8
6.0	29	25	24	26	3
3.1	31	37	25	31	4
1.0	57	61	58	59	2
0.78	46	61	58	55	8
0.48	55	50	59	55	5
0.21	47	53	51	50	3
0.11	30	38	34	34	4

H₂ Sensor	Recovery time				
% H₂	sample 1	sample 2	sample 3	AVG	STD
9.6	48	43	46	46	3
6.0	48	47	47	47	1
3.1	36	31	28	32	4
1.0	51	50	52	51	1
0.78	59	55	56	57	2
0.48	43	45	51	46	4
0.21	44	46	50	47	3
0.11	32	38	40	37	4

Figure 3.7. Schematic representation of the mechanism involved with the H_2 sensor.

Figure 3.8. Current-time plot of H₂ switch device measured at -0.3V in the presence of N₂ initially and in the presence of various concentrations of H₂ (H₂ on) and 100% N₂ (H₂ off) as indicated (A) for 9.6, 6.0, 3.1% H₂ and (B) for 1.0% H₂ of a different device.

Figure 3.9. (A) AFM image of a finger of the Au IDA electrode with electrodeposited polyphenol (10 cycles) after scratching away an area of the polymer film with the AFM tip and (B) A cross-sectional analysis of the scratched area of the polyphenol film showing that the thickness is approximately 5.9 nm in this area. The thickness range of this area and other areas analyzed show that the film thickness ranges from about 4-10 nm. The film is therefore thick enough to prevent electronic conductance through the Pd/polyphenol/E2 junction, but thin enough that a connection can be made between Pd and E2 through the porous polyphenol when the Pd expands in volume as PdH_x in the presence of H_2 . Some open areas of the polyphenol film are also labeled in the image.

Figure 3.10. Schematic representation of the mechanism involved with the H_2 switch.

junctions, is supported by three facts. First, we observe a similar threshold detection of about 1.0% H₂, which is where the transition from α -phase to β -phase Pd occurs.^{45,87,91,151} Below this threshold, the volume expansion of PdH_x is not sufficient to form a direct connection to E2. Second, the current of the “H₂ switch” device above 1.0% H₂ is the same order of magnitude as the current (10⁻³ to 10⁻⁴ A) of the directly-connected Pd in the “H₂ sensor” (Figure 3.5 and Table 3.4-3.5), which strongly suggests that direct contact occurs for the “H₂ switch”. Third, current-voltage curves of the “H₂ switch” in the presence of H₂ exhibit ohmic behavior as does the directly-connected Pd in Figure 3.1C, making it unlikely that changes in Schottky barriers lead to the switching behavior. Devices fabricated with polyphenol using 4 or 5 electrochemical cycles also operated as “H₂ switches” (Figure 3.11), but with <100% success. The response and recovery times are generally shorter than 10-cycle devices (Table 3.6-3.7), which we attribute to faster penetration of PdH_x through the thinner, more porous polyphenol film.

3.4. CONCLUSIONS

In summary, we demonstrate a combination of Pd electrodeposition and polyphenol electropolymerization at microgap electrode arrays for controlled H₂ sensing and switching behavior. While the results here are specific to the Pd/H₂ system, the general strategy of electrochemically controlling metal/organic/metal junctions at microgap electrodes should find broad use in a number of sensing, nanoelectronics, and molecular electronics applications.⁸⁵

Table 3.4. Final currents at different H ₂ concentrations for each trial of the different "H ₂ switch" devices.					
10 cycles of Phenol					
sample 1	Trial 1	Trial 2	Trial 3		
% H ₂	Final current	Final current	Final current	AVG	STD
9.6	1.29×10 ⁻³	1.28×10 ⁻³	1.25×10 ⁻³	1.27×10 ⁻³	0.02×10 ⁻³
6.0	1.28×10 ⁻³	1.28×10 ⁻³	1.20×10 ⁻³	1.25×10 ⁻³	0.04×10 ⁻³
3.1	1.11×10 ⁻³	1.15×10 ⁻³	1.10×10 ⁻³	1.12×10 ⁻³	0.03×10 ⁻³
sample2	Trial 1	Trial 2	Trial 3		
% H ₂	Final current	Final current	Final current	AVG	STD
9.6	2.47×10 ⁻³	2.48×10 ⁻³	/	2.48×10 ⁻³	0.01×10 ⁻³
6.0	1.89×10 ⁻³	2.19×10 ⁻³	/	2.04×10 ⁻³	0.21×10 ⁻³
3.1	1.73×10 ⁻³	2.20×10 ⁻³	/	1.97×10 ⁻³	0.33×10 ⁻³
sample 3	Trial 1	Trial 2	Trial 3		
% H ₂	Final current	Final current	Final current	AVG	STD
9.6	4.19×10 ⁻³	3.66×10 ⁻³	/	3.93×10 ⁻³	0.37×10 ⁻³
6.0	3.86×10 ⁻³	2.11×10 ⁻³	/	2.99×10 ⁻³	1.24×10 ⁻³
3.1	3.56×10 ⁻³	1.96×10 ⁻³	/	2.76×10 ⁻³	1.13×10 ⁻³
1.0	3.37×10 ⁻³	/	/		
sample 4	Trial 1	Trial 2	Trial 3		
% H ₂	Final current	Final current	Final current	AVG	STD
9.6	1.19×10 ⁻³	/	/	/	/
6.0	1.18×10 ⁻³	/	/	/	/
3.1	1.11×10 ⁻³	/	/	/	/
sample 5	Trial 1	Trial 2	Trial 3		
% H ₂	Final current	Final current	Final current	AVG	STD
9.6	2.25×10 ⁻³	/	/	/	/
6.0	1.98×10 ⁻³	/	/	/	/
3.1	0.35×10 ⁻³	/	/	/	/
1.0	0.28×10 ⁻³	/	/	/	/

Table 3.4 (continued) Final currents at different H₂ concentrations for each trial of the different "H₂ switch" devices studied.

5 cycles Phenol					
sample 1	Trial 1	Trial 2	Trial 3		
% H₂	Final current	Final current	Final current	AVG	STD
9.6	0.42×10^{-3}	0.38×10^{-3}	/	0.40×10^{-3}	0.02×10^{-3}
6.4	0.26×10^{-3}	0.30×10^{-3}	/	0.28×10^{-3}	0.03×10^{-3}
3.1	0.17×10^{-3}	0.22×10^{-3}	/	0.19×10^{-3}	0.04×10^{-3}
sample2	Trial 1	Trial 2	Trial 3		
% H₂	Final current	Final current	Final current	AVG	STD
9.6	3.12×10^{-3}	2.97×10^{-3}	/	3.05×10^{-3}	0.11×10^{-3}
6.0	3.06×10^{-3}	2.88×10^{-3}	/	2.97×10^{-3}	0.13×10^{-3}
3.1	2.87×10^{-3}	2.56×10^{-3}	/	2.72×10^{-3}	0.22×10^{-3}
4 cycles Phenol					
sample 1	Trial 1	Trial 2	Trial 3		
% H₂	Final current	Final current	Final current	AVG	STD
9.6	0.74×10^{-3}	0.72×10^{-3}	/	0.73×10^{-3}	0.01×10^{-3}
6.0	0.45×10^{-3}	0.45×10^{-3}	/	0.45×10^{-3}	0.004×10^{-3}
3.1	0.30×10^{-3}	0.29×10^{-3}	/	0.29×10^{-3}	0.006×10^{-3}
sample2	Trial 1	Trial 2	Trial 3		
% H₂	Final current	Final current	Final current	AVG	STD
9.6	1.56×10^{-3}	1.49×10^{-3}	/	1.53×10^{-3}	0.05×10^{-3}
6.0	1.54×10^{-3}	1.36×10^{-3}	/	1.45×10^{-3}	0.13×10^{-3}
3.1	0.60×10^{-3}	0.62×10^{-3}	/	0.61×10^{-3}	0.02×10^{-3}

Table 3.5. Average final currents at various H ₂ concentrations for “H ₂ switch” devices as a function of number of electrochemical cycles in phenol.						
Sample	10 Cycles Phenol		5 Cycles Phenol		4 Cycles Phenol	
% H₂	AVG	STD	AVG	STD	AVG	STD
9.6	2.56×10 ⁻³	1.32×10 ⁻³	1.72×10 ⁻³	1.32×10 ⁻³	1.13×10 ⁻³	0.39×10 ⁻³
6.0	2.09×10 ⁻³	0.88×10 ⁻³	1.62×10 ⁻³	1.34×10 ⁻³	0.95×10 ⁻³	0.50×10 ⁻³
3.1	1.95×10 ⁻³	0.82×10 ⁻³	1.45×10 ⁻³	1.26×10 ⁻³	0.45×10 ⁻³	0.16×10 ⁻³
1.0	0.62 ×10 ⁻³ *	0.48×10 ⁻³ *	/	/	0.22 ×10 ⁻³ #	/

10 cycles phenol – The average is from three devices (Samples 1, 2, and 3).

* The value at 1.0% H₂ represent the average for two devices (Samples 4 and 5).

5 and 4 cycles phenol – The average is from two different devices (Samples 1 and 2).

The value at 1.0% H₂ is for one device (Sample 2).

Figure 3.11. Current-time plots for "H₂ Switch" devices with a film on Electrode 2 electrodeposited using polyphenol (A) 4 cycles and (B) 5 cycles, measured at -0.3 V in the presence of N₂ initially and in the presence of various concentrations of H₂ (H₂ on) and 100 % N₂ (H₂ off) as indicated. Devices with 4 and 5 cycles of polyphenol generally have faster response/recovery times, but not a 100% success rate as 10 cycle phenol devices do.

Table 3.6. Response and recovery times at different H ₂ concentrations for each trial of the different "H ₂ switch devices studied.										
10 Cycles Phenol										
Sample 1	Response time					Recovery time				
% H ₂	Trial 1	Trial 2	Trial 3	AVG	STD	Trial 1	Trial 2	Trial 3	AVG	STD
9.6	29	44	36	36	8	172	182	157	170	13
6.0	34	48	39	41	7	131	153	72	119	42
3.1	46	28	41	38	25	67	36	52	52	16
Sample 2	Response time					Recovery time				
% H ₂	Trial 1	Trial 2	Trial 3	AVG	STD	Trial 1	Trial 2	Trial 3	AVG	STD
9.6	22	24	/	23	1	68	76	/	72	6
6.0	40	55	/	48	11	67	73	/	70	4
3.1	56	35	/	46	15	72	41	/	57	22
Sample 3	Response time					Recovery time				
% H ₂	Trial 1	Trial 2	Trial 3	AVG	STD	Trial 1	Trial 2	Trial 3	AVG	STD
9.6	29	12	/	21	12	144	222	/	183	55
6.0	21	20	/	21	1	48	117	/	83	49
3.1	72	41	/	57	22	108	51	/	80	40
Sample 4	Response time					Recovery time				
% H ₂	Trial 1	Trial 2	Trial 3	AVG	STD	Trial 1	Trial 2	Trial 3	AVG	STD
9.6	27	/	/	/	/	76	/	/	/	/
6.0	32	/	/	/	/	63	/	/	/	/
3.1	48	/	/	/	/	48	/	/	/	/
1.0	830	/	/	/	/	27	/	/	/	/
Sample 5	Response time					Recovery time				
% H ₂	Trial 1	Trial 2	Trial 3	AVG	STD	Trial 1	Trial 2	Trial 3	AVG	STD
9.6	13	/	/	/	/	12	/	/	/	/
6.0	16	/	/	/	/	10	/	/	/	/
3.1	19	/	/	/	/	9	/	/	/	/
1.0	24	/	/	/	/	8	/	/	/	/

Table 3.6 (continued). Response and recovery times at different H ₂ concentrations for each trial of the different "H ₂ switch devices studied.								
5 Cycles Phenol								
Sample 1	Response time				Recovery time			
% H ₂	Trial 1	Trial 2	AVG	STD	Trial 1	Trial 2	AVG	STD
9.6	20	16	18	3	32	29	31	2
6.0	26	25	26	1	15	15	15	0
3.1	24	27	26	2	32	25	29	5
Sample 2	Response time				Recovery time			
% H ₂	Trial 1	Trial 2	AVG	STD	Trial 1	Trial 2	AVG	STD
9.6	8	15	13	5	26	25	26	4
6.0	9	14	13	2	17	34	26	11
3.1	33	32	33	1	26	17	22	4
4 Cycles Phenol								
Sample 1	Response time				Recovery time			
% H ₂	Trial 1	Trial 2	AVG	STD	Trial 1	Trial 2	AVG	STD
9.6	11	12	12	1	31	22	27	6
6.0	13	11	12	10	27	25	26	1
3.1	20	15	18	4	5	7	6	1
Sample 2	Response time				Recovery time			
% H ₂	Trial 1	Trial 2	AVG	STD	Trial 1	Trial 2	AVG	STD
9.6	7	9	8	1	22	23	23	1
6.0	14	6	10	6	22	23	23	1
3.1	23	22	23	1	15	11	13	3
1.0	110	/	/	/	9	/	/	/

Table 3.7. Average response and recovery times for H₂ switch devices to various concentrations of H₂ as a function of number of electrochemical cycles in phenol.

H ₂ Switch	Response time					
Sample	10 Cycles Phenol		5 Cycles Phenol		4 Cycles Phenol	
% H ₂	AVG	STD	AVG	STD	AVG	STD
9.6	27	9	16	5	10	2
6.0	37	14	20	10	11	1
3.1	47	9	30	5	21	4
1.0	426*	570*	/	/	110 [#]	/
H ₂ Switch	Recovery time					
Sample	10 Cycles Phenol		5 Cycles Phenol		4 Cycles Phenol	
% H ₂	AVG	STD	AVG	STD	AVG	STD
9.6	142	61	29	4	25	3
6.0	91	25	21	7	25	2
3.1	63	15	26	5	10	5
1.0	17*	13*	/	/	9 [#]	/

10 cycles phenol – The average is from three devices (Samples 1, 2, and 3).

* The value at 1.0% H₂ represents the average for two devices (Samples 4 and 5).

5 and 4 cycles phenol – The average is from two different devices (Samples 1 and 2).

The value at 1.0% H₂ is only for one device (Sample 2).

CHAPTER IV

ELECTROCHEMICAL FABRICATION OF METAL/ORGANIC/METAL JUNCTIONS FOR MOLECULAR ELECTRONICS AND SENSING APPLICATIONS

²A simple electrochemical approach was used for fabricating electrode/metal nanowire/(molecule or polymer)/electrode junctions for sensing or molecular electronics applications. The procedure for fabricating these molecule-based devices involves electropolymerization of phenol or chemisorption of alkanethiols on one set of electrodes (E1) and electrodeposition of Ag metal nano/micro-wires on a second electrode (E2) which is ~5 μm away from E1. Under appropriate deposition conditions, Ag nanowires grow from E2 and cross over to E1, forming a E1/(molecule or polymer)/Ag nanowire (NW)/E2 junction. The junction resistance was controlled by 1) electrodepositing polyphenol of varied densities on E1, and 2) assembling alkanethiols of different chain lengths on E1. Ag NWs at high resistance E1/polyphenol/Ag NW/E2 junctions functionalized with Pd monolayer protected clusters (MPCs) responded fast and reversibly to H_2 concentrations as low as 0.11% in a nitrogen carrier gas by a resistance decrease, likely due to volume expansion of the Pd nanoparticles, demonstrating the use of these electrochemically-fabricated junctions for gas sensing applications.

4.1. INTRODUCTION

It has been demonstrated that the properties of individual, small groups, or thin films

² Reprinted with permission from Dasari, R.; Ibañez, F. J.; Zamborini, F. P. *Langmuir* **2011**, 27, 7285-7293

of molecules are useful for electronic and photoelectronic-based devices, such as switches and sensors. Molecule-based electronic devices have been heavily explored in recent years as this approach may someday overcome the size limitations of the current silicon based electronics technology. It is possible to fabricate a wide variety of functional devices using molecules based on their electronic, optical, magnetic, thermoelectronic and molecular recognition properties. Understanding the electronic properties of molecules is essential to fabricate future molecule-based devices. It is therefore necessary to easily and reproducibly prepare metal/molecule/metal junctions in order to study the fundamental electronic and structural properties of the molecules within the junction.

Various techniques have been used for fabricating and studying the electronic properties of metal/molecule/metal junctions. Scanning probe microscopy (SPM) methods, such as scanning tunneling microscopy (STM)⁶⁷⁻⁷³ and conducting tip atomic force microscopy (CT-AFM)⁷⁴⁻⁷⁸ are common. Several groups used STM to monitor the electronic properties of alkanethiols, alkylamines, xylyldithiols, phenylene ethylene oligomers, and conjugated and nitro-substituted self assembled monolayers (SAMs). CT-AFM was used to study the electronic properties of Langmuir-Blodgett films and alkanethiol self assembled monolayers (SAMs). In scanning probe based techniques the measurements are localized to nanometer- or atomic-scale areas. One can select the area and make direct electronic measurements of the molecules supported on a substrate. These techniques can be used to study the electronic properties down to single molecules. SPM based methods are excellent for making several measurements and obtaining statistical data fairly quickly but they do suffer from some disadvantages. With STM

there are questions about the tip-molecule contact. The presence of solvent or the water meniscus can affect the electronic properties observed using STM break junctions.⁷⁹⁻⁸⁰ Factors such as substrate roughness, tip chemistry, extended tip usage, and radius of the tip that is in contact with the monolayer influence the measurements and analysis using AFM. It is also difficult to maintain the same tip conditions throughout the experiment. Above all, scanning probe based techniques are not practical for a working device, but are useful for fundamental studies.

Some other strategies for fabricating metal/molecule/metal junctions include mercury junctions,¹⁵²⁻¹⁵⁴ nanopores,¹⁵⁵⁻¹⁵⁸ and crossed wire junctions.¹⁵⁹⁻¹⁶¹ Mercury junctions are easy to fabricate, which allows one to measure the electronic properties of a statistically significant number of junctions. Also, these junctions have less chances of forming short circuits; the high surface tension of mercury reduces the probability of metal penetration into the SAM. Unfortunately, mercury junctions are mechanically unstable and impractical for incorporation into a microelectronic device. In metal capped nanopores, the adsorbed SAM in the junction is highly ordered and defect free, since the contact area is smaller than the domain size of the SAM employed. This method involves the vapor deposition of a top contact electrode. Vapor-deposited noble metals can lead to the formation of electrical shorts and reactive metals can lead to the distortion of the molecules. A highly conducting polymer poly(3,4-ethylenedioxythiophene):poly(4-styrenesulphonic acid) has been used between a SAM and top electrode to minimize the formation of such shorts.¹⁶² The presence of hydrophobic alkanethiols makes it difficult to use them in the processing of the hydrophilic (PEDOT:PSS) and the electronic properties tend to be irreproducible. Also, several measures have to be taken during the

deposition of the top electrode to minimize damage to the SAM. The fabrication of metal nanopore junctions involves e-beam lithography, which is expensive and tedious.

Crossed wire junctions involve multiple steps, including the synthesis and assembly of the wires followed by electrode contact formation.

Molecules can also be assembled between pre-formed nano-gap electrodes to form metal/molecule/metal junctions. Electromigration formed break junctions,⁵³⁻⁵⁵ mechanically controlled break junctions,⁵⁶⁻⁵⁸ optical lithography,⁵⁹ and molecular lithography⁶⁰ are examples of techniques used to fabricate nano-gap electrodes. All of these approaches are somewhat tedious, have low yields, and lack reproducibility.

Here we present a simple benchtop electrochemical method to fabricate metal/organic/metal junctions. Other electrochemical methods for fabricating metal contacts to molecules have also been reported in the literature. For example, nanowire junctions were previously formed by electrodepositing metal contacts in the pores of polycarbonate membranes.⁸¹⁻⁸³ Molecules were also assembled between nanogap electrodes fabricated electrochemically using a method termed on-wire lithography⁶¹ or nanowire lithography.⁶² These approaches require assembling of nanowire junctions or striped metal nanowires between the contact electrodes. Tao and coworkers developed an electrochemical deposition/etching method to fabricate atomic or molecular scale nanogap electrodes and studied the sensing and electronic properties of polymers in the gap.⁶³⁻⁶⁶ Recently, Campbell and coworkers reported an electrochemical method for fabricating metal/molecule/metal junctions.⁸⁴⁻⁸⁵ In their method, they fabricated two electrodes separated by 20 nm by e-beam lithography. They coated one electrode with a SAM and deposited Pt on the second electrode to form a metal/SAM/Pt junction. Our

approach described here is similar to Campbell and coworkers, except that we use 5 μm gap interdigitated array electrodes fabricated by photolithography and form metal/molecule/metal junctions by deposition of a SAM or polymer at one electrode followed by electrochemical deposition of Ag nanowires (NWs) at the other. The benefit of our approach is a smaller contact area of the junction since Ag NWs serve as one of the electrodes, cheaper and massively parallel fabrication, since we use photolithography, and great versatility in the types of electrodes and molecules that can be placed in the junction. We recently used this approach to fabricate H_2 sensing and switching devices based on electrodeposited Pd at the junction.¹⁶³ Here we fabricated molecular junction devices with electrochemically-deposited Ag NWs. We describe the electronic properties of these junctions and a H_2 sensing application made possible by functionalizing the Ag NWs with Pd monolayer-protected clusters (MPCs). This represents a first step towards our goal of using electrochemistry and self-assembly to form massively parallel and reproducible molecular electronics and sensing devices.

4.2. EXPERIMENTAL

Electrode wiring and cleaning procedure. Refer to Chapter 2. section 2.2.2.

Electrodeposition of Ag nanowires (NWs). Ag was electrodeposited on electrode 1 (E1). Refer to Chapter 2. section 2.3.3. for details.

Fabrication of molecule-based devices. Fabrication of E1/Ag NW/polyphenol/E2 junctions involve electrodeposition of phenol on electrode 2 (E2) followed by Ag electrodeposition on electrode 1 (E1). Refer to Chapter 2. section 2.3.8 for details. In order to fabricate E1/AgNW/SAM/E2 junctions, an alkanethiolSAM was assembled on

both the electrodes E1 and E2. Later the SAM was desorbed from E1. Finally Ag was electrodeposited on E1. Refer to Chapter 2, section 2.3.3. for details.

Functionalization of Ag NWs with Pd MPCs. Ag NWs were functionalized with Pd MPCs by placing devices with E1/Ag NW/polyphenol (10cycles)/E2 junctions in a toluene solution of Pd MPCs. Refer to Chapter 2, section 2.3.6. for the details.

Hydrogen sensing experiments. Refer to Chapter 2, section 2.3.7. for details.

4.3. RESULTS AND DISCUSSION

Electrochemical fabrication of Ag Nanowire junctions. Figure 4.1 shows the procedure for the fabrication of Ag Nanowires across the microgap electrodes (see Chapter 2, section 2.3.3. for details). In short 6.0×10^{-5} C of Ag was electrodeposited onto electrode E1, allowing it to make contact to electrode E2. Figure 4.2A shows an SEM image of the entire Au electrode IDA device where we selectively electrodeposited Ag on E1. Under our diffusion-controlled deposition conditions (~ 300 mV negative of the onset of Ag deposition), and 0.005M AgNO₃ Ag deposited in the form of wire- or needle-like structures and made a direct connection between the E1 and E2 electrodes. The expanded SEM image of the same device in Figure 4.2B shows three different E1/Ag NW/E2 connections (labeled as 1, 2, and 3). The average number of connections per device was 6 ± 2 and the apparent diameter of the Ag NWs ranged from 100 to 300 nm based on the top view SEM images.

Electronic properties of E1/Ag NW/E2 junctions. Figure 4.2C shows a current-voltage (i-V) plot of the same device in air before and after Ag deposition. The i-V plot after deposition displays ohmic behavior with a current of 15 mA at -1.0 V ($R=67 \Omega$). Based on the known conductivity of Ag ($630,000 \Omega^{-1}\text{cm}^{-1}$), the current observed for the

Figure 4.1. Fabrication of Ag nanowires across microgap electrodes.

Figure 4.2. (A) SEM image (top view) of the entire IDA after electrodeposition of Ag on electrode 1, E1 (B) Expanded SEM image of circled region of Figure 1A. (C) i-V curve from -1 to 1 V at 100 mV/s scan rate and (D) Current-time plot at -0.3V of the IDA.

device corresponds to a contact area of only $\sim 34 \times 34 \text{ nm}^2$ assuming a square contact region. This shows that the actual contact area is much smaller than the apparent micron-sized contact area observed from the top view SEM images. Alternatively, the contact area could be larger, but the junction contains some other source of resistance, such as a thin Ag oxide layer, adventitious organic contamination, or some other barrier to electron transfer between the Ag nanowire and E2. Figure 4.2D shows the current-time plot in air for the same device at -0.3 V for 100 s. The 4.58 mA current remained constant with time as expected for ohmic behavior. Table 4.1 shows the device current, resistance, apparent connections and contact area based on the resistance for all of the devices studied. Figure 4.3 shows a plot of the contact area as a function of the expected current (as a log plot) calculated from the Ag bulk conductivity for comparison to the observed current of our devices.

Electronic properties of E1/Ag NW/organic film/E2 junctions. Figure 4.4A and 4.4B show the procedures for the fabrication of E1/Ag NW/polyphenol/E2 and E1/AgNW/SAM/E2 junctions, respectively (See Chapter 2. section 2.3.4. experimental section for details). Figure 4.5A shows an SEM image of the entire Au IDA electrode device where we electrodeposited polyphenol (10 cycles) on one set of electrodes (E2) and Ag on the other electrode (E1). Figure 4.6A shows an expanded SEM image of a portion of the same device. Ag again deposited as needle-like structures on the edges of the Au IDA electrodes and made connections between the E1 and E2 electrodes. The SEM image in Figure 4.6A shows one particular connection. No Ag deposition occurred on the polyphenol-coated E2 electrode since it was not connected as the working electrode and the polyphenol served as a resistive layer inhibiting contact between the

Table 4.1. Number of connections, current, resistance, and contact area for the devices with Ag nanowires at microgap electrodes.					
Sample	# of fingers in IDA	# of apparent connections (top view)	Current at -1V from i-V curve (A)	Resistance at 1V (Ω)	Contact area nm²
1	14	8	0.015	62.5	34×34
2	10	4	0.021	47.6	41×41
3	14	7	0.007	142.9	23×23

Figure 4.3. Calculated contact area as a function of the log(current) based on bulk Ag conductivity.

Figure 4.4. Method for fabricating an A) E1/AgNW/polyphenol/E2 junction and B) E1/Ag NW/SAM/E2 junction.

Figure 4.5. SEM images of entire array of Au IDA electrode with (A) 10 cycles of polyphenol on one set of electrodes (E2) and Ag on the other set of electrodes (E1) and (B) Hexanethiol on E2 and Ag on E1.

Figure 4.6. SEM image of a region of an Au IDA device with an E1/Ag NW/polyphenol (10 cycles)/E2 junction (B) i-V curve and (C) current-time plot of the same device.

Ag and E2.

Figure 4.6B shows an i-V curve of the device before (background) and after fabrication of the E1/Ag NW/polyphenol (10 cycles)/E2 junction. The current is slightly above background and there is some hysteresis in the i-V curve. The current passing through the device was approximately 8 orders of magnitude lower when compared to the current of a E1/AgNW/E2 junction where there is no polyphenol on E2. The polyphenol electrodeposited at E2 has a low electronic conductivity and serves as a resistive barrier to electron transport from the Ag wire to E2. The expected current for the ~5 nm thick polyphenol film,¹⁶³ assuming an average contact area of $33 \times 33 \text{ nm}^2$ from Table 4.1, is $1.5 \times 10^{-16} \text{ A}$ based on the known conductivity of polyphenol.¹⁵⁰ The larger current above the background and above that expected for pure polyphenol shows there is some small leakage current through the polyphenol film; the source is unknown.

We studied the electronic properties of E1/Ag NW/polyphenol/E2 junctions prepared by electropolymerization of polyphenol with a varied number of cycles ranging from 3 to 10. With an increasing number of cycles, the polyphenol film becomes slightly thicker, but more importantly, more dense.¹⁶⁴ These films typically contain defects that become filled with an increasing number of electrochemical cycles.¹⁶⁴ Table 4.2 shows the currents measured at -1.0 V from i-V curves for the different devices fabricated with varied electropolymerization cycles. The Table shows a general trend that the current was larger for devices prepared with fewer cycles, but the device currents were not completely reproducible. For example, three different devices prepared with 3 polyphenol cycles on E2 displayed currents of $1.61 \times 10^{-2} \text{ A}$, $9.25 \times 10^{-5} \text{ A}$, and $1.64 \times 10^{-8} \text{ A}$. The current varied by 6 orders of magnitude, showing large device irreproducibility for this number

Table 4.2. Currents displayed at -1.0 V for devices with different number of electropolymerization cycles of phenol on E2 and Ag on E1. Values in the parantheses are junction resistances in MΩ.						
sample	3 Cycles	4 Cycles	5 Cycles	6 Cycles	7 Cycles	10 Cycles
1	9.25×10^{-5} A (1.08×10^{-2})	8.60×10^{-9} A (1.16×10^2)	1.68×10^{-9} A (5.95×10^2)	0.80×10^{-10} A (1.25×10^3)	1.13×10^{-10} A (8.85×10^3)	8.20×10^{-10} A (1.22×10^3)
2	1.61×10^{-2} A (6.21×10^{-4})	0.82×10^{-10} A (1.22×10^3)	7.56×10^{-4} A (1.32×10^{-3})	/	/	8.01×10^{-11} A (1.25×10^4)
3	1.64×10^{-8} A (0.61×10^2)	2.49×10^{-9} A (4.02×10^2)	1.35×10^{-9} A (7.41×10^2)	/	/	2.06×10^{-10} A (4.85×10^3)

of cycles. For 4 and 5 cycles of polyphenol, the currents were generally in the 10^{-9} to 10^{-10} A range, except for one device, which was 10^{-4} A for 5 cycles. Devices with 6 or more cycles of polyphenol were all in the 10^{-10} to 10^{-11} A range, showing a large resistance that is more reproducible. This procedure clearly does not lead to precise control over the Ag NW/polyphenol/E2 junction, but the number of polyphenol cycles does offer some general control over the resistance over 9 orders of magnitude.

The electronic properties as a function of the number of polyphenol cycles can be classified into four different types of junctions. Type I includes devices that are highly insulating with currents in the 80-800 pA range at -1.0 V (12500 M Ω to 1250 M Ω). Based on these low currents, the expected contact area ranges from 0.00252×0.00252 nm² to 0.00797×0.00797 nm² (Figure 4.3). With a contact area smaller than 1 atom, we conclude that the Ag NW was not in direct contact with E2 in this case. Electron transport likely occurred through the polyphenol film at relatively large distances. Devices with 6 to 10 polyphenol cycles displayed currents in this range. Type II devices include those that displayed currents and calculated contact areas ranging from μ A to nA levels and 0.28×0.28 nm² to 0.0089×0.0089 nm² respectively. In this range, there could be atomic-scale contacts formed between the Ag and E2 or electron transport may occur through the polyphenol film at relatively short distances by tunneling. Devices with 4 to 5 polyphenol cycles showed higher probability for nA currents. Type III devices include devices with mA to μ A currents. Based again on the expected current as a function of contact area, we believe that currents in the mA to μ A range represent nano-scale or atomic-scale shorts formed between the Ag NW and E2 through the defective polyphenol layer. Type IV devices include those devices with currents ranging from mA to A, where

the Ag NW is in direct nanoscale contact with E2 as for E1/Ag/E2 devices. Figure 4.7 shows a schematic of these four types of devices.

Electronic properties of E1/Ag NW/SAM/E2 junctions. Figure 4.5B shows an SEM image of an entire Au IDA electrode device where we chemisorbed hexanethiol on E2 and electrodeposited Ag on E1. Figure 4.8A shows a SEM image of a region of the same device. Ag deposited preferentially on the edges and made connections between the electrodes as with the other junctions. Figure 4.8B shows the i-V curve before and after fabrication of the E1/Ag NW/hexanethiol/E2 junction. The current passing through this device was 2.0×10^{-7} A at -1.0 V ($R=5$ M Ω). The hexanethiol SAM on E2 blocks the Ag NW from making direct contact with E2, resulting in lower currents displayed by the device compared to E1/Ag NW/E2 junctions.

Figure 4.8C shows the current-time plot in air for three different devices with alkanethiols of varying chain length incorporated in the junction. Note that the current for the junction with hexanethiol is different from that in frame B because it is a different device. Table 4.3 shows the currents displayed at -0.3V by multiple devices with different alkanethiols in the junction between Ag and the Au E2 electrode. Unfortunately the device currents were not very reproducible. Devices with currents in the mA range likely represent those where the Ag NW penetrated the SAM and formed a direct nanoscale contact with E2. The number of devices with currents in the mA range, also shown as % of shorts in Table 4.3, generally decreased as the chain length of the SAM increased following the order of Butanethiol (75%) > Hexanethiol (23%) > Dodecanethiol (13%) ~ Octadecanethiol (17%). The longer chainlength alkanethiols formed a more uniform and well-ordered monolayer, decreasing the probability of the Ag

Figure 4.7. Four types of junctions: I) Transport through polyphenol at long distances, II) Transport through polyphenol at short distances (tunneling) III) Atomic scale shorts and IV) Nanoscale contacts.

Figure 4.8. (A) SEM image of a region of an Au IDA device with an E1/Ag NW/hexanethiol/E2 junction (B) i-V curve and (C) Current-time plot of the same device.

Table 4.3. Currents (A) displayed at -0.3V by devices with alkanethiols of different chain lengths on E2 and Ag on E1 in the junction. Values in the parenthesis are junction resistances in M Ω .				
Sample	Butanethiol	Hexanethiol	Dodecanethiol	Octadecanethiol
1	$1.5 \times 10^{-2} (2.0 \times 10^{-5})$	$1.1 \times 10^{-10} (2.7 \times 10^3)$	$8.0 \times 10^{-12} (3.7 \times 10^4)$	$9.8 \times 10^{-11} (3.1 \times 10^3)$
2	$1.9 \times 10^{-2} (1.6 \times 10^{-5})$	$1.2 \times 10^{-8} (0.2 \times 10^2)$	$9.6 \times 10^{-12} (3.1 \times 10^4)$	$9.6 \times 10^{-12} (3.1 \times 10^4)$
3	$1.9 \times 10^{-2} (1.6 \times 10^{-5})$	$7.3 \times 10^{-10} (4.1 \times 10^2)$	$5.2 \times 10^{-11} (5.8 \times 10^3)$	$9.0 \times 10^{-11} (3.3 \times 10^3)$
4	$2.1 \times 10^{-2} (1.4 \times 10^{-5})$	$6.6 \times 10^{-12} (4.5 \times 10^4)$	$1.7 \times 10^{-9} (2.0 \times 10^2)$	$7.8 \times 10^{-10} (3.8 \times 10^2)$
5	$1.6 \times 10^{-2} (1.9 \times 10^{-5})$	$7.5 \times 10^{-8} (0.4 \times 10^1)$	$8.0 \times 10^{-11} (3.7 \times 10^3)$	$4.2 \times 10^{-11} (7.1 \times 10^3)$
6	$1.9 \times 10^{-2} (1.6 \times 10^{-5})$	$2.7 \times 10^{-8} (1.1 \times 10^1)$	$9.5 \times 10^{-11} (3.1 \times 10^3)$	$1.59 \times 10^{-2} (1.9 \times 10^{-5})$
7	$8.0 \times 10^{-11} (3.7 \times 10^3)$	$7.1 \times 10^{-12} (4.2 \times 10^4)$	$2.4 \times 10^{-9} (1.2 \times 10^2)$	/
8	$5.8 \times 10^{-11} (5.2 \times 10^3)$	$3.0 \times 10^{-8} (0.1 \times 10^2)$	$1.20 \times 10^{-2} (2.5 \times 10^{-5})$	/
9	/	$1.1 \times 10^{-11} (2.7 \times 10^4)$	/	/
10	/	$1.1 \times 10^{-10} (2.7 \times 10^3)$	/	/
11	/	$1.2 \times 10^{-2} (2.0 \times 10^{-5})$	/	/
12	/	$2.3 \times 10^{-2} (2.0 \times 10^{-5})$	/	/
13	/	$1.2 \times 10^{-2} (2.0 \times 10^{-5})$	/	/
%	75	23	13	17
shorts				

NW penetrating through defect sites within the SAM. The expected currents for electron transport through hexanethiol and dodecanethiol molecules based on literature reports of their single molecule resistance and our average contact area of $33 \times 33 \text{ nm}^2$ is $8.8 \times 10^{-7} \text{ A}$ and $2.6 \times 10^{-9} \text{ A}$, respectively. While our devices were irreproducible, there were a few devices where the current was within the expected current levels, suggesting that these electrochemically-fabricated junctions may be useful for measuring the electronic properties of molecules if we can reduce the probability of forming shorts and improve the reproducibility.

Hydrogen Sensing. One of our long-term goals is to use molecular devices for electronic-based sensing applications. Here we demonstrate a H_2 sensor device as a proof-of concept. Figure 4.9 shows the procedure for the fabrication of the H_2 sensor using a device with an E1/Ag NW/polyphenol(10 cycles)/E2 junction (details are provided in Chapter 2. section 2.3.7). Figure 4.10A shows a zoomed-in SEM image of a bare, smooth Ag wire. Figure 4.10B shows an image of a different Ag NW that was decorated with octylamine-coated Pd MPCs using the procedure shown in Figure 4.9. The surface of the Ag NW was no longer smooth, confirming the attachment of the $\sim 3 \text{ nm}$ diameter Pd MPCs. The small bright spots on the surface of the wire correspond to the Pd MPCs, which are not well resolved because the size is close to the resolution limit of the SEM. Figure 4.10C shows an image of an Ag NW decorated with Pd MPCs after exposure to H_2 gas from 9.6 to 0.11%. The nanoparticles appear larger and rougher after H_2 sensing due to the morphological changes that are common following volume expansion and contraction of Pd that occurs upon exposure to H_2 .^{45,91}

Figure 4.9. Method for the fabrication of a H₂ sensor.

Figure 4.10. SEM images of three different devices showing (A) A bare Ag NW, (B) An Ag NW functionalized with Pd MPCs, and (C) An Ag NW functionalized with Pd MPCs after hydrogen exposure.

Figure 4.11A shows i-V curves of the device before and after attachment of Pd MPCs to the Ag NWs in the E1/AgNW/polyphenol/E2 device. The current increased from 1.0×10^{-10} to 2.2×10^{-7} A at -1.0 V after attaching Pd MPCs to the Ag NWs. This suggests that not only do the Pd MPCs attach on the surface of the Ag wires but also insert into the Ag NW/polyphenol/E2 junction to facilitate electron transport between the Ag wire and E2 (Figure 4.9). Figure 4.12 shows an i-V curve of the device after placing it in toluene (no nanoparticles) for 20 min. There is no change in current after placing the device into toluene only, which shows that the increased current observed after placing the device in Pd MPCs is due to the insertion of the Pd nanoparticles into the junction, not due to toluene (solvent) exposure.

Figure 4.11B shows the current-time plot measured at -0.3 V for the device before and after exposure to 100% H₂. The current was initially stable at $\sim 1.0 \times 10^{-7}$ A in 100% N₂. After we changed the environment to 100% H₂ at ~ 100 s, the current increased from 1.0×10^{-7} A to $\sim 4.0 \times 10^{-7}$ A before dropping back to and stabilizing at $\sim 3.7 \times 10^{-7}$ A. This irreversible response to the first exposure of H₂ is common for Pd-based H₂ sensing devices. The expansion of Pd upon formation of PdH_x induces irreversible strain on the Pd lattice that leads to an irreversible morphology and resistance change. After this initial exposure to H₂, often referred to as conditioning, the Pd then responds reversibly as the H₂ adsorbs into the Pd lattice (as PdH_x) and desorbs in the presence of N₂. Figure 4.11C shows the current at -0.3 V as a function of time in the presence of 100% N₂ (H₂ “off”, ○) and various H₂ concentrations (H₂ “on”, ●) after the initial exposure to 100% H₂ in Figure 4.11B. The current was initially stable in the presence of N₂, increased in the presence of various H₂ concentrations, and now reversibly decreased back to the baseline

Figure 4.11. (A) i-V curves of the device with E1/Ag NW/polyphenol/E2 junction before and after attachment of Pd MPCs, (B) Current-time plot measured at -0.3V in the presence of N_2 initially and then in the presence of 100% H_2 (C) Current-time plot measured at -0.3V in the presence of N_2 initially and in the presence of various concentrations of H_2 (H_2 on) and 100% N_2 .

Figure 4.12. i-V curves after placing a device with 10 cycles of phenol on E2 and Ag on E1 in toluene with no exposure to Pd MPCs. There is no change in current showing toluene has no effect on the junction.

current when placed in 100% N₂. This is likely due to the formation of PdH_x as the Pd nanoparticles react with H₂. We believe the volume expansion of Pd as it reacts with H₂ to form PdH_x leads to better contact between the Ag wire and the E2 electrode, leading to a current increase in the device (see Figure 4.13). The device responded reversibly from 9.6% down to 0.11% H₂. The sensor showed a non-linear response between 1.0% and 3.1% H₂ which is due to the α - to β - phase-transition that occurs during PdH_x formation and above 3.1% the sensor approached saturation. The response was fairly linear from 0.0-1.0% H₂, where primarily α phase PdH_x exists.¹⁶⁵ Figures 4.14A and 4.14B show calibration curves for three different devices for the entire range of 0.0 to 9.6% H₂ and the linear range from 0.0 to 1.0% H₂. The average theoretical limit of detection obtained from the 0 to 1.0% H₂ calibration curves is $0.07 \pm 0.05\%$ H₂ (Table 4.4). Table 4.4 shows the percent response for the different concentrations of H₂ for three different devices. The average response and recovery times at 1.0% H₂ are 21 ± 4 s and 42 ± 6 s, respectively. Table 4.5 shows percent responses for different trials for three different devices as a function of H₂ concentration. Frame A in Figure 4.15 shows an i-V curve after placing the device with Ag NWs grown across E2 (no polyphenol) in Pd MPCs for 20 min. In this case, there was no change in current after attaching Pd MPCs to the directly connected Ag nanowires. Frame B in Figure 4.15 shows a current-time plot for the same device in the presence of 100% H₂. The device did not show any change in current in the presence of H₂ confirming that a Ag NW/polyphenol/E2 junction is necessary for detecting H₂ upon attachment of Pd MPCs. The low initial current is necessary in order to observe a significant resistance change upon volume expansion of Pd when it forms PdH_x. When the conductivity is initially large, due to

Figure 4.13. Mechanism involved in H_2 sensing.

Figure 4.14. Calibration curves showing percent responses vs H₂ concentrations for three different devices with E1/Ag NW/polyphenol(10 cycles)/E2 junctions functionalized with Pd MPCs (A) The entire range of 0.11-9.6% and (B) The linear range of 0.11 to 1.0%.

Table 4.4. Percent responses for three different devices as a function of H ₂ concentration along with the linear value of the slope and limit of detection for each device.					
Sample	1	2	3		
% H₂	% Response	% Response	% Response	AVG	STDEV
9.6	22.67	42.97	41.1	35.60	11.19
6.0	21.01	40.31	35.96	32.43	10.13
3.1	17.73	35.81	30.61	28.05	9.31
1.0	8.76	18.75	15.65	15.50	3.33
0.48	2.78	5.63	5.29	4.57	1.56
0.21	1.02	3.79	3.77	2.86	1.59
0.11	0.19	2.94	2.77	1.97	1.54
Sample	1	2	3		
Linear slope(% res.%H₂)	12.59	14.96	18.16	15.24	2.80
Limit of detection (%H₂)	0.02	0.13	0.07	0.07	0.05

Table 4.5. Percent responses for different trials for three different devices as a function of H₂ concentration.

Sample 1	% Response				
% H ₂	Trial 1	Trial 2	Trial 3	AVG	STDEV
9.6	21.21	21.96	24.84	22.67	1.92
6.0	19.75	20.22	23.05	21.01	1.79
3.1	16.36	17.64	19.19	17.73	1.42
1.0	8.40	9.10	8.78	8.76	0.34
0.48	2.87	2.68	2.78	2.78	0.10
0.21	1.17	0.76	1.13	1.02	0.23
0.11	0.24	0.14	0.18	0.19	0.05
Sample 2	% Response				
% H ₂	Trial 1	Trial 2	Trial 3	AVG	STDEV
9.6	40.32	40.26	48.34	42.97	4.65
6.0	37.67	37.53	45.74	40.31	4.70
3.1	32.38	32.52	42.52	35.81	5.81
1.0	17.72	18.19	20.34	18.75	1.40
0.48	5.36	5.17	6.36	5.63	0.64
0.21	3.61	3.88	3.88	3.79	0.16
0.11	2.84	/	3.03	2.94	0.13
Sample 3	% Response				
% H ₂	Trial 1	Trial 2	Trial 3	AVG	STDEV
9.6	40.87	41.35	41.1	41.11	0.24
6.0	35.60	36.09	36.2	35.96	0.32
3.1	30.56	30.97	30.3	30.61	0.34
1.0	16.56	15.26	15.13	15.65	0.79
0.48	5.01	5.76	5.12	5.29	0.41
0.21	4.22	3.47	3.62	3.77	0.40
0.11	/	2.77	/	2.77	0.00

Figure 4.15. (A) i - V curve after attaching Pd MPCs to bare Ag NWs. There is no change in the current. The black line is the background before deposition of Ag NWs. (B) The current as a function of time in 100% N₂ initially and then after exposure to 100% H₂ (H₂ on). The device did not show any response to H₂.

directly connected Ag, the attachment of 3 nm diameter Pd MPCs and the formation of PdH_x has no effect on the device conductivity. We note that several other groups have used Pd in hydrogen sensing devices. Some examples include Pd wires,^{45,91,163,165-166} nanotubes,¹⁶⁷⁻¹⁶⁸ nanoparticles,^{90,145,147} Pd decorated SWCNTs,¹⁶⁹⁻¹⁷¹ and multilayer graphene nanoribbon networks functionalized with Pd nanoparticles.¹⁷² Some of these examples detect H₂ with millisecond responses at the low ppm level. While our sensor has a detection limit of 700 ppm H₂, the device is easy to construct, can be easily mass produced fairly cheaply, has a fast response, and detects H₂ well below the explosive limit of 4% (40000 ppm).

Our results also demonstrate that these electrochemically-fabricated metal-organic-metal junctions can be functionalized for chemiresistive sensing applications in general. We envision several other possible strategies with different types of molecules and materials in the junction for future chemical and biological sensing applications.

4.4. CONCLUSIONS

We demonstrated a simple method for fabricating nano/micro wire-based and molecule-based devices using electrochemistry and self-assembly. The approach is simple, fast and can be applied to any metal or molecule that can be electrodeposited or self-assembled on electrodes, leading to the fabrication of a wide variety of devices with metal/organic/metal junctions. We inserted Pd nanoparticles into E1/Ag NW/polyphenol/E2 junctions for sensing H₂ to demonstrate the potential use of this method for sensing applications. This method could easily be extended for a wide range of other sensing applications. Device reproducibility is clearly an area with need for improvement. The reproducibility at this stage is not good enough for this method to be

used to obtain statistical data involved in fundamental unexplored molecular electronics studies. We are currently working to improve the reproducibility and control over the junctions for this application. However, we do believe our simple, fast, and low cost approach is useful for the fabrication of molecular sensing and electronics devices based on known chemistry from the literature.

CHAPTER V

ELECTROCHEMICAL FABRICATION OF TWO TERMINAL NANOSCALE RESISTIVE SWITCHES

Here we report a simple electrochemical approach for fabricating two terminal resistive switching devices. This method involves electrodeposition of Ag nanowires (NWs) onto one set of electrodes (E1) that connected to a second set of electrodes (E2) of an interdigitated array of electrodes with a 5 μm separation. Then Ag was removed from electrodes E2 by electrochemical oxidation, leading to a break in the connection between the Ag NWs and E2. The initially high solid state resistance (off state) in air decreased dramatically (on state) at potentials greater than ± 2 V due to Ag filament formation between the Ag NW and E2 electrode. These filament based switching devices exhibited an on/off ratio over 10^4 and endurance of at least 10^2 cycles.

INTRODUCTION

New device concepts and architectures are needed to overcome the physical and economic limitations of current semiconductor devices.¹¹⁵ In this regard two terminal resistive switches are devices that can be used for ultra high density memory storage or logic applications.¹¹⁶ In general, resistive switching device structures consists of an insulating or semiconducting material that is sandwiched between two metal electrodes. For example, chalcogenides (Ag-Ge-Se, AgS, and CuS, etc.),¹¹⁷⁻¹¹⁹ metal oxides (Cu-

doped SiO, WO₃, ZrO, and TiO₂, etc.),¹²⁰⁻¹²² and amorphous Si (a-Si)^{123-124,136} have been sandwiched between two electrodes. Resistive switching in these devices is attributed to the formation of conductive filaments in the insulating layer due to joule heating,¹²⁶ electrochemical processes in binary oxides,¹²⁹ redox processes in ionic conductors such as oxides and chalcogenides,¹²⁸⁻¹²⁹ and field-assisted drift/diffusion of ions in TiO or a-Si.¹³² Devices consisting of molecules sandwiched between electrodes also exhibit hysteretic switching.¹⁷³ Previously, amorphous Si based switches exhibited on/off ratios greater than 10³, fast programming speed (5ns), and long endurance (10⁶ cycles), but e-beam lithography was involved in the fabrication of these devices.¹²⁵ Most of the methods used to make these devices are tedious, often requiring e-beam lithography, costly, or impractical.

Resistive switching is also observed in metallic nanogap electrodes due to metal electromigration when the gap width is less than about 13 nm.¹³⁷⁻¹³⁸ These devices are simple in structure as they do not need any material to be sandwiched between the electrodes. They also exhibited on/off ratios over 10³, but they usually require a high voltage (10V) for switching. Also, fabrication of nano gap electrodes often leads to the formation of shorts (device failure). Penner and coworkers fabricated sub 5 nm nanogaps using lithographically patterned nanowire electrodeposition (LPNE) and demonstrated that these nanogaps get connected by ramping the voltage.¹⁷⁴ Here we describe a simple electrochemical method to fabricate metal nanogap electrodes that exhibit resistive switching behavior. Our method is very simple, highly parallel, doesn't need any material to be sandwiched between the electrodes, exhibits on/off ratios over 10⁴, and has long endurance (10² cycles). More importantly the device requires low voltage (± 2 V) for

resistance switching compared to other nanogap electrodes.

EXPERIMENTAL SECTION

Electrode wiring and cleaning procedure. Refer to Chapter II for details.

Fabrication of Resistance Switching Devices. Figure 5.1 shows a schematic representation of the steps involved in the electrochemical fabrication of the resistive switch. In step 1, 6.0×10^{-5} C of Ag was deposited on electrode 1 (E1), leading to ohmic contact between E1 and E2 by the Ag NW. In step 2, the Ag from E2 was removed by electrochemical oxidation by cycling from -0.3V to 0.5V in 0.1M H₂SO₄. In step 3, we applied a potential of ± 5 V to the electrode E2. Refer to Chapter 2 for full details.

RESULTS AND DISCUSSION

Figure 5.2A shows the cyclic voltammogram of an Au IDA electrode in 5 mM AgNO₃ in aqueous 0.1 M H₂SO₄. The peaks at ~ -0.1 and ~ -0.05 V represent Ag reduction and oxidation respectively. The dashed line indicates the potential used to electrodeposit Ag NWs. Figure 5.2B shows a current-voltage (i-V) plot of the device in air before and after Ag deposition (Potential sign is on Au E2 electrode). The i-V plot after deposition displays ohmic behavior with a current of 20 mA at -1.0 V ($R=67 \Omega$) as described in Chapter III. Based on the known conductivity of Ag ($630,000 \Omega^{-1}\text{cm}^{-1}$), the current observed for the device corresponds to a contact area of $\sim 34 \times 34 \text{ nm}^2$ assuming a square contact region.¹⁹⁵ Figure 5.2C shows a linear sweep voltammogram (LSV) from -0.1 to 0.6V at a scan rate of 100 mV/s of an Au IDA device electrodeposited with Ag on E1 obtained in 0.1M H₂SO₄ by hooking only E2 to the potentiostat. The Ag stripping peak was not symmetrical since the current dropped quickly to zero as soon as the contact between the Ag and the Au electrode, E2, was broke.

Figure 5.1. Schematic representation of the procedure involved in the fabrication of a resistance switch.

Figure 5.2. A) Cyclic voltammogram of Au IDA in 5 mM AgNO_3 in 0.1M H_2SO_4 (Ag wire was used as reference electrode) (B) i-V plot in air from 1 to -1 V of the device where Ag was selectively electrodeposited on E1 (C) Linear sweep voltammogram (LSV) obtained in 0.1M H_2SO_4 by hooking only E2 to the potentiostat of Au IDA device electrodeposited with Ag on E1, (Ag/AgCl was used as reference electrode) (D) i-V plot from 1 to -1 V of the same device in air before Ag electrodeposition and after stripping Ag from E2 and (E) Schematic representation showing the oxidation of Ag and formation of the nanogap. Scan rate 100 mV/s.

Figure 5.2D shows a current-voltage (i-V) plot of the device in air before Ag electrodeposition and after stripping Ag from E2. The current decreased back to background over the ± 1.0 V range, which confirmed the breaking of contact and formation of a nanogap between the Ag NW and E2. Figure 5.2E is a schematic representation showing the oxidation of Ag. Ag that is in contact with E2 becomes oxidized first, creating a nanogap. Region 1 and 2 correspond to those shown in Figure 5.2C.

Figure 5.3A shows a top view SEM image of the entire Au electrode IDA device after selective electrodeposition of Ag onto E1. Ag deposited in the form of wire- or needle like structures and made a direct connection between the E1 and E2 under our diffusion-controlled deposition conditions (~ 300 mV negative of the onset of Ag deposition). The average number of connections per device was 6 ± 2 and the apparent diameter of the Ag NWs ranged from 100 to 300 nm based on the top view SEM images as described in Chapter IV. Figure 5.3B shows a side-view SEM image of a portion of an Au IDA electrode device after selective electrodeposition of Ag onto E1. Side view SEM images show that the Ag deposits both vertically and horizontally from E1 preferentially at the edges of the electrodes and apparent connections viewed from the top as in Figure 5.3A may not actually be in contact with E2. Figure 5.4A shows a zoomed in top view SEM image of one of the AgNWs represented by the red open circle in Figure 5.3A. Figure 5.4B shows the same AgNW from the side. Other features shown in the image are labeled (A,C,D and E). The top view SEM image (Figure 5.4A) shows that the contact area is in the micron range where as the side view image (5.4B) shows that the Ag NW is actually hovering over the electrode and a smaller portion of it is actually

Figure 5.3 A) SEM image of entire Au IDA electrode where Ag was selectively electrodeposited on E1. (B) Side view of a portion of the same device.

Figure 5.4. Expanded SEM images of one wire labeled as wire 1 in Figure 5.3A. A) Top view and B) Side view and, C) Zoomed in image of the circled portion Frame B showing that the contact region is less than 100 nm.

in contact with electrode 2. This shows that the actual contact area is much smaller than the apparent micron-sized contact area observed from the top view SEM images, consistent with currents that correlate to nanoscale contacts. This and other possible sources of high contact resistance likely explain the small contact area calculation.

We took a device which had only one AgNW that connected electrodes E1 and E2 after electrodepositing Ag on E1 and imaged it after stripping Ag from E2 to observe the breakage of contact between the Ag NW and E2 and the formation of a nanogap. Figure 5.5A shows a top view SEM image of a device after stripping Ag from E2. From the top view the Ag NW appeared connected to E2. But the current displayed by this device at -1V is in 10^{-10} A range which indicates that the Ag NW is not in contact with E2. Figure 5.5B and 5.5C show the zoomed in SEM images of the same Ag NW from two different side views. The side views reveal that the Ag NW was disconnected from E2 in support of the *i*-V data (Figure 5.2D).

Figure 5.6 shows an *i*-V curve of the same device from 5 to -5 V collected by sweeping the potential from 0 to -5 to 5 and back to 0V as indicated by the black arrows at a scan rate of 100 mV/s. While scanning the potential from 0 to -5V the device switched from a low current state to high current state once the applied potential was more negative than -3V, eventually reaching 9.0×10^{-5} A at -5 V (Figure 5.6). The device also exhibited switching behavior when the potential was scanned in the opposite polarity from 0 to 5V, but the current was much lower (0.2×10^{-5} A at 5V). Table 5.1 shows the currents displayed by three different devices at -5 and 5V. The current at -5V is greater than the current at the 5V by 5 to 20 times, indicative of diode-like behavior.

Figure 5.7A and 5.7B show *i*-t plots of the device while the voltage was stepped

Figure 5.5. SEM images of an Ag NW after stripping Ag from E2 from three different angles. A) Top view, B) and C) are side views from different angles.

Figure 5.6. i-V plot in air from 5 to -5 V of the resistive switching device (nanogap electrode after stripping Ag from E2). Scan rate 100 mV/s.

Table 5.1. Currents displayed by three different resistance switching devices at -5V and 5V.			
Sample	-5V	5V	-5V/5V ratio
1	0.9×10^{-5} A	0.2×10^{-5} A	5
2	4.0×10^{-5} A	0.2×10^{-5} A	20
3	1.0×10^{-5} A	0.1×10^{-5} A	10

Figure 5.7. i-t plot of the resistive switching device when the potential was stepped between (A) 0.1 V and 5V and (B) 0.1V and -5V.

between 0.1V and 5V and 0.1V and -5V respectively. The device switched from a low current state to a high current state with a potential change from 0.1V to 5V or -5V. The current increased 5-6 orders of magnitude from $\sim 4.0 \times 10^{-11}$ A (25000 M Ω) to $\sim 0.96 \times 10^{-5}$ A (0.1 M Ω) and from $\sim 4.0 \times 10^{-11}$ A to $\sim 2.0 \times 10^{-6}$ A (0.5 M Ω) when the potential was switched from 0.1V to -5V and 5V respectively. Step 3 in Figure 5.1 shows the proposed mechanism involved in the switching. When a voltage (± 5 V) is applied it generates a high electric field which drives the Ag atoms from the AgNW to the Au E2 electrodes which results in the formation of an Ag filament. This Ag filament acts as a conductive pathway for the electrons resulting in a much lower “on state” resistance as compared to the “off state”, in which the filament is not formed. Figure 5.8A shows i-V curves of the device scanned several times from 0 to -5V. As the number of scans increased the potential at which the device switched from the low current to high current state decreased. This is consistent with observations made by Hsuing *et al*, who observed that the Ag filament is structurally unstable and breaks into a number of particles until there is less effective spacing between the electrodes.¹⁷⁵ Lower voltage is required to switch the device from the higher “off state” resistance to lower “on state” resistance in subsequent scans. Eventually, the “on state” occurred near -1.0 V. After a month, the device exhibited switching behavior but the current in the “on” state decreased by two orders of magnitude (See Figure 5.8B).

CONCLUSIONS

In summary, we demonstrated a simple electrochemical approach for fabricating two terminal resistive switching devices. They exhibited on/off ratios over 10^4 and long endurance (10^2 cycles). With further improvements in the device structure to ensure high

Figure.5.8 A) i-V curves from 0 to -5 V of the resistance switch device scanned several times and (B) i-t plot when the potential is stepped between 0.1V to 5V. This was obtained a month after the device was fabricated.

programming speeds we believe that these devices would be strong candidates for future nonvolatile memory applications.

CHAPTER VI

TIP ENHANCED RAMAN SPECTROSCOPY ON PLANAR SURFACES

Here we describe a simple approach to fabricate E1/Ag Nanowire (NW)/Aminothiophenol (ATP)/E2 junctions by combining self-assembly and metal electrodeposition at micro gap electrodes in order to characterize the Raman enhancement properties of the electrochemically-fabricated Ag NWs. In this method we assemble the ATP on electrode (E2) and electrodeposit Ag on the opposite electrode (E1) of an Au IDA electrode. The electrodeposited Ag grows in the form of nanowires and makes nanoscale contact to form E1/Ag NW/ATP/E2 junctions. The presence of the Ag nanowire at the junction leads to strong Raman scattering of the ATP molecules within the nanojunction leading to enhancement factors estimated as high as 10^6 - 10^8 . The Ag NWs act similar to tip enhanced Raman spectroscopy (TERS) but on a planar surface. The TERS enhancement at several junctions within a device allowed us to determine the extent of contact between the Ag NW and the ATP SAM. With this approach we could detect ATP molecules diluted by 1000 with hexanethiol molecules on a SAM within the junctions.

INTRODUCTION

There is renewed interest in surface-enhanced Raman Spectroscopy (SERS) as it has reached single molecule sensitivity.¹⁷⁶⁻¹⁷⁸ “Hot spots” generated at junctions between plasmon-coupled metal nanoparticles are responsible for the strong enhancement of

Raman signals.¹⁷⁹⁻¹⁸⁰ Since SERS is a noninvasive detection method it can be applied for the identification of biological molecules such as DNA and proteins.¹⁸¹⁻¹⁸² In order to develop SERS into an effective analytical tool there is a need to fabricate well defined, reproducible and controlled hot spots.

A few examples of such hot spots fabricated by several other groups are lithographically fabricated surfaces,^{143,183-184} nanoparticle dimers,¹⁸⁵⁻¹⁸⁷ aggregates,¹⁸⁸⁻¹⁸⁹ nanowire bundles,¹⁹⁰⁻¹⁹¹ and crossed and parallel nanowire systems.¹⁹² With a simple geometry of a sharp metallic tip over planar surfaces, known as tip enhanced Raman spectroscopy (TERS), sufficient enhancements for single molecule detection have been achieved. Nanogap electrodes and crossed and parallel nanowire systems have recently been explored for Raman enhancement in order to better understand the electronic properties of molecules in the junction.

Here we describe an approach to fabricate E1/Ag nanowire (NW)/aminothiophenol (ATP)/E2 junctions which lead to strong Raman enhancement of the ATP that is sandwiched between the two metals. One benefit of this approach is that the hot spots can be easily observed under an optical microscope. Hence, effective SERS measurements can be achieved with high efficiency. Crossed and parallel nanowire systems can also be readily monitored by an optical microscope, but the fabrication of these systems is tedious as it involves a micromanipulator and contacts have to be made to the nanowires in order to measure the electronic properties of the molecules. Junctions fabricated by our method serve as hot spots for Raman enhancements, can be easily monitored by an optical microscope, and can potentially be used as a platform for performing molecular conductivity and SERS measurements simultaneously.

EXPERIMENTAL SECTION

Electrode wiring and cleaning procedure. Refer to Chapter II. section 2.2.2. for details.

Fabrication of Electrode/AgNW/ATP(monolayer and submonolayer)/Electrode junctions. Figure 6.1 shows a schematic representation of the steps involved in the fabrication of Electrode/AgNW/ATP/Electrode junctions. These junctions were fabricated using the procedure as reported in Chapter 2.3.8. Briefly, the method involves the formation of a monolayer or submonolayer of ATP on both electrodes followed by desorption of ATP from electrode E1. Finally Ag was electrodeposited onto electrode E1. Submonolayers of ATP are formed by placing the electrode overnight in ATP solutions containing hexanethiol at concentrations 9,99 and 999 times large than ATP. The hexanethiol/ATP solutions were prepared by adding 1, 0.1, and 0.01 ml of 2 mM ATP solution to 9, 9.9, and 9.99 mL of 2 mM hexanethiol solution. The ATP: hexanethiol ratio in these solutions was 1:9, 1:99, and 1:999, respectively.

RESULTS AND DISCUSSION

Figure 6.2A shows an SEM image of an entire Au IDA device where we chemisorbed ATP on E2 and electrodeposited Ag on E1. Ag NWs deposited preferentially on the edges of E1 and made several connections between the two electrodes leading to the formation of E1/AgNW/ATP/E2 junctions as previously described. Numbers 1 to 8 in Figure 6.2A represent the number of E1/AgNW/ATP/E2 junctions in the device. Figure 6.2B shows a zoomed in SEM image of the circled portion in Figure 6.2A. It shows one of the Ag NWs connecting the two electrodes of the device shown in Figure 6.2A. The circled portion in Figure 6.2B shows the E1/AgNW/ATP/E2 junction from which the

Figure 6.1. Schematic representation of method for fabricating E1/Ag NW/ATP(monolayer or submonolayer)/E2 junction.

Figure. 6.2. (A) SEM image of the entire 14 finger Au IDA device with (E1)Au/ATP/Ag NW/Au(E2) junctions. The red circle represents the area that is shown as an expanded SEM image in frame B. These devices contain multiple Ag NWs crossing the electrodes. The average number of E1/Ag NW/ATP/E2 junctions on the device based on top view SEM images is 6 ± 2 . (B) Expanded SEM image of the circled region in frame A. The red circle represents the (E1)Au/ATP/Ag NW/Au(E2) junction. This is one of 8 junctions on this device, labeled as number 3.

Raman spectrum was collected. In order to confirm that the enhanced Raman signal for ATP in the junction is due to Ag NWs, we obtained spectra from the junction and at locations away from the junction. Figure 6.3A to 6.3E show the optical images from the Raman spectrometer of the same junction as shown in Figure 6.2B. The red open circles in the SEM image and the cross hairs in the optical images indicate the region where the spectrum was collected. Figure 6.4A shows the SERS spectra of the ATP molecules obtained from different regions of the device represented by the red open circles in the SEM image of Figure 6.3. Figure 6.4B shows the zoomed in SERS spectra obtained from regions B to E represented by the red open circles in the SEM image. The SERS signal of the ATP molecules from the edges and the surface of the Au electrodes or directly on the Ag wire, (Regions B to E) is extremely weak and non-existent. In contrast, the signal from the nanojunction (region A) is strong, showing that the Ag NW significantly enhanced the Raman scattering from ATP relative to the other areas. The Ag NWs act in a similar fashion as a tip in TERS, but in a planar chip format. We observed similar Raman modes for the ATP molecule as reported previously.¹⁹³ Table 6.1 shows the vibrational assignment for selected Raman bands of ATP, although these have recently been attributed to a dimer (4, 4' dimercaptoazobenzene) by Tian and co-workers.

Figure 6.5A shows the SERS spectra obtained from devices with E1/AgNW/ATP/E2 junction, E1/Ag NW/E2 junction (no ATP) and ATP chemisorbed on E1 and E2 (no Ag NW), respectively (See Figure 6.5B for device illustrations). We observed signal for ATP molecules only from the devices with ATP molecules present in the junction. The device which did not have ATP molecules in the junction (E1/AgNW/E2) did not show any signal confirming that the signal we observed from the junction corresponds to ATP.

Figure 6.3. A) SEM image of one E1/Ag NW/ATP/E2 junction. Red open circles represent the regions from which the Raman spectra were obtained and (B to F) represent the optical images of the same E1/Ag NW/ATP/E2 junction as in Frame A with the cross hairs. Cross hairs represent the area from where the Raman spectra were collected.

Figure 6.4. A) SERS spectra (632.8 nm laser) of ATP molecules obtained at different regions on the electrode device represented by the red open circles in Figure 6.4A and B) Zoomed in spectra collected from B-E regions.

Table 6.1. Selected SERS bands of ATP with their vibrational assignment.

1071	SC str and NH₂ rock
1139	CH bend
1187	CN str and CH rock
1389	CC str in phenyl ring and CH rock and NH₂ rock
1434	CC str in phenyl ring and NH₂ rock
1576	CC str in phenyl ring and NH₂ bend

Figure 6.5. A) SERS spectra obtained from devices with E1/Ag NW/ATP/E2 junction (Black spectra), E1/Ag NW/E2 junction (no ATP) (Red spectra) and ATP chemisorbed on E1 and E2(no Ag NW) (Green spectra), B) Scheme showing the devices with I) E1/Ag NW/ATP/E2 junction, II) ATP chemisorbed on E1 and E2(no Ag NW).

There was no signal above the noise level for ATP molecules from the device where ATP was chemisorbed on E1 and E2 with no Ag NW present. This conclusively shows that the electrochemically-fabricated Ag NWs are responsible for the Raman enhancement of ATP molecules in the junction.

We tested the reproducibility of the Raman enhancement from these Ag NW junction. We first tested the reproducibility of the same junction. Figure 6.6 shows the SERS spectra obtained three times from the same region of the same E1/Ag NW/ATP/E2 junction. The deviation in the signal of the Raman band at 1587 cm^{-1} was 6% for the same region. We also tested the reproducibility of different E1/Ag NW/ATP/E2 junctions within the same device and in different devices. Table 6.2 shows the intensity of the Raman signal for different E1/Ag NW/ATP/E2 junctions within the same device and in different devices. The intensity of the Raman band at 1587 cm^{-1} varies from 3000-60000 for different junctions. This large deviation could be due to differences in Ag morphology and different contact between Ag and ATP. Figure 6.7A to 6.7H shows the optical images and Figure 6.7I to 6.7P shows the SERS spectra of different E1/Ag NW/ATP/E2 junctions, corresponding to the junctions numbered as 1 to 8 in the SEM image shown in Figure 6.2A. The higher signal for some junctions likely corresponds to closer contact and a more enhanced plasmon field at the AgNW contact. Thus the SERS enhancement of several junctions within a device can be used to determine the extent of contact between the AgNW and ATP SAM. It is necessary to estimate the Raman enhancement factor for these Ag NWs to determine their potential use for analytical applications. The enhancement factor (EF) is calculated using the formula given below:

$$EF = (I_{\text{SERS}} \times N_{\text{bulk}}) / (I_{\text{bulk}} \times N_{\text{SERS}})$$

Figure 6.6. SERS spectra of ATP molecules obtained from the same spot of the E1/Ag NW/ATP/E2 junction three times.

Table 6.2. Intensities of the Raman signal for different E1/Ag NW/ATP/E2 junctions within the same device and in different devices. Values in the parantheses indicate current displayed by the device at -1V. Enhancement factor calculated for the Raman band at 1580 cm^{-1} .

	Wave number (cm^{-1})		Enhancement factor	
			Background 1	Background 2
Ag Nanowire	1071	1580	0.9×10^6	0.9×10^7
Device 1 ($0.96 \times 10^{-9}\text{A}$) wire1	2733	2998	1.0×10^6	1.0×10^7
wire 2	4941	3191	1.9×10^6	1.9×10^7
wire 3	5553	6323	2.1×10^6	2.1×10^7
wire 4	5987	6981	2.3×10^6	2.3×10^7
wire 5	15998	7664	3.1×10^7	3.1×10^8
wire 6	18246	10074	3.5×10^6	3.5×10^7
Device 2 ($4.53 \times 10^{-9}\text{A}$) wire 1	4491	11526	4.7×10^6	4.7×10^7
wire 2	7633	15459	4.9×10^6	4.9×10^7
wire 3	9276	16206	1.0×10^7	1.0×10^8
wire 4	11680	32750	1.0×10^7	1.0×10^8
Device 3 ($0.13 \times 10^{-7}\text{A}$) wire 1	38535	59214	1.8×10^7	1.8×10^8
Range	2733 - 38535	2998 - 59214	0.9×10^6 - 1.8×10^7	0.9×10^7 - 1.8×10^8

Figure 6.7. Frames A to H represent the optical images of different E1/Ag NW/ATP/E2 junctions numbered as 1 to 8 in the SEM image shown in Figure 6.2A. Cross hairs represent the area from where the Raman spectra were collected and Frames I to P represent the SERS spectra obtained from the respective E1/Ag NW/ATP/E2 junctions.

Figure 6.7. Continued. Frames A to H represent the optical images of different E1/Ag NW/ATP/E2 junctions numbered as 1 to 8 in the SEM image shown in Figure 6.2A. Cross hairs represent the area from where the Raman spectra were collected and Frames I to P represent the SERS spectra obtained from the respective E1/Ag NW/ATP/E2 junctions.

Figure 6.7. Continued. Frames A to H represent the optical images of different E1/Ag NW/ATP/E2 junctions numbered as 1 to 8 in the SEM image shown in Figure 6.2A. Cross hairs represent the area from where the Raman spectra were collected and Frames I to P represent the SERS spectra obtained from the respective E1/Ag NW/ATP/E2 junctions.

where I_{sers} is the intensity of the Raman band (we use 1576 cm^{-1}) obtained from the junction, and I_{bulk} is the intensity of the Raman signal obtained away from the junction, either from the edge of the Au electrode or in the middle of the electrode where ATP is chemisorbed but Ag NW is absent. N_{bulk} is the number of ATP molecules giving rise to the Raman signal in the absence of the metal and N_{sers} is the number of molecules of ATP molecules giving rise to the signal in the presence of the metal. It is reported that each ATP molecule occupies 0.2 nm^2 . The laser illumination area has a radius of $1 \text{ }\mu\text{m}$, or area $3.14 \times 10^6 \text{ nm}^2$. This means that there are approximately 1.57×10^7 ATP molecules in the illumination area, N_{bulk} . If we consider that the spot is the same in the presence of the metal, then N_{sers} is equal to N_{bulk} . Next, we estimate I_{bulk} to be about 10 counts based on spectra B and E (Figure 6.4), obtained at the electrode edge. These would be lower in the middle of the electrode. The highest I_{sers} from Table 6.2 is about 60,000 counts. From these values, the EF would be:

$$\text{EF} = (I_{\text{sers}} \times N_{\text{bulk}}) / (I_{\text{bulk}} \times N_{\text{sers}}) = (60,000 \times 1.57 \times 10^7) / (10 \times 1.57 \times 10^7) = 6000 = 6.0 \times 10^3$$

If we consider I_{bulk} is 10 counts for a $1 \text{ }\mu\text{m}$ radius spot size in the absence of metal, the intensity at the metal site is approximately $60,000 - 10$, or $59,990$. We then estimate the number of molecules within the metal site from the Ag NW contact area, which is based on the resistance of a bare Ag NW junction ($32 \text{ nm} \times 32 \text{ nm}$ or 1024 nm^2). The number of ATP molecules in 1024 nm^2 is 5120. The EF would then be

$$\text{EF} = (59,990 \times 1.57 \times 10^7) / (10 \times 5120) = 1.8 \times 10^7$$

We estimate the EF range is $10^6 - 10^8$ considering that I_{bulk} ranges from indistinguishable to ~ 100 counts. Inaccuracies in the AgNW contact area could further effect the EF factor. Recently, it was reported that SERS enhancements of $10^8 - 10^{10}$ are sufficient for

single molecule detection.¹⁹⁴ This is important as it suggests we are in the range close to single molecule sensitivity. Others have reported EF values of 10^4 - 10^6 for AgNRs and NWs.

Figure 6.8 shows the SERS spectra of the ATP molecules obtained from E1/AgNW/ATP/E2 junctions with different coverages of ATP (10, 100 and 1000 fold diluted with hexanethiol). Figure 6.8 shows Raman spectra at junctions with SAMs formed from 1:9, 1:99, 1:999 ATP: hexanethiol ratios. Table 6.3 shows the intensities of the signal for the Raman band at 1587 cm^{-1} obtained from the different junctions. The intensity of the signal for the Raman band at 1587 cm^{-1} ranged from 200 to 2000, 200 to 2500, and 50 to 200 for the 1:9, 1:99, 1:999 mixed ATP:hexanethiol SAMs respectively. No signal above noise level was observed for samples with 1:999 ATP:hexanethiol SAMs. Although the Raman intensities vary considerably, there is strong correlation where ATP was diluted with 10000 hexanethiol molecules. If we consider median there is a correlation between the median Raman intensity and the concentration of ATP in the SAM. Based on the estimated $32\text{nm}\times 32\text{nm}$ contact area, the 1:999 ATP:hexanethiol SAM would contain about 5 ATP molecules. This is only approaching single molecule SERS, but the contact area is only an estimate.

CONCLUSIONS

In summary, we described a simple approach to fabricate E1/Ag Nanowire (NW)/Aminothiophenol (ATP)/E2 junctions by combining self-assembly and metal electrodeposition at micro gap electrodes. The electrodeposited Ag grew in the form of nanowires and made nanoscale contact to form E1/Ag NW/ATP/E2 junction. The presence of the Ag nanowire at the junction led to strong Raman scattering of the

Figure 6.8. SERS spectra of ATP molecules diluted by A) 10 B) 100 and C) 1000 with hexanethiol molecules within the junction.

Table 6.3. Intensities of the signal for the Raman band at 1587 cm^{-1} obtained from different junctions (for pure ATP, ATP diluted with hexanethiol molecules).

		ATP:hexanethiol			
Sample		Pure ATP	1:9	1:99	1:999
Sample 1	Wire 1	2998	210	250	50
	Wire 2	6323	675	1783	87
	Wire 3	6981	1995	1654	270
	Wire 4	7664	1687	/	50
	Wire 5	15459	/	/	/
	wire 6	32750	/	/	/
Sample 2	Wire 1	3191	1935	2491	234
	Wire 2	10074	825	1824	173
	Wire 3	11526	916	528	87
	Wire 4	16206	1820	/	56
	Wire 5	/	776	/	142
	Wire 6	/	1492	/	/
	Wire 7	/	1659	/	/
Sample 3	Wire 1	59214	492	1278	68
	Wire 2	/	1702	384	134
	Wire 3	/	1824	662	185
	Wire 4	/	/	248	97
	Wire 5	/	/	825	139
Median		10740	1492	794	115

molecules within the nanojunction leading to enhancement factors estimated as high as 10^6 - 10^8 . The SERS enhancement of several junctions within a device allowed us to determine the extent of contact between the AgNW and ATP SAM. Submonolayer coverages of SAMs, specifically ATP molecules diluted by ~1000 with hexanethiol molecules could be detected within the junctions by SERS. In order to correlate the electronic properties of molecules with structural changes in the future, we would use these devices as a platform for measuring conductivity and SERS measurements simultaneously potentially with single (or few) molecule sensitivity.

CHAPTER VII

SIMULTANEOUS CONDUCTIVITY AND ENHANCED RAMAN SPECTROSCOPY MEASUREMENTS AT ELECTROCHEMICALLY-FABRICATED METAL-ORGANIC- METAL NANOFUNCTIONS

Here we describe a simple approach to fabricate E1/Ag Nanowire (NW)/Aminothiophenol (ATP)/E2 junctions which can be used as a platform for performing simultaneous conductivity and surface-enhanced Raman spectroscopy measurements. In this method we assemble the ATP on one set of electrodes (E2) and electrodeposit Ag on the opposite set of electrodes (E1) of an Au interdigitated array (IDA) electrode device with a 5 μm separation. The electrodeposited Ag grows from E1 in the form of NWs and makes nanoscale contact to E2 to form E1/Ag NW/ATP/E2 junctions. The presence of the Ag NW at the junction leads to strong Raman scattering, within the nanofunction, leading to enhanced Raman signals of the ATP molecule within the junction. This approach allows spectroscopic characterization of the molecules in the junction while simultaneously monitoring the electronic properties. This could potentially allow us to better understand what controls the electronic properties at the molecular level. We correlated the electronic properties of the junction to the enhanced Raman spectroscopy to demonstrate the usefulness of our fabrication method for molecular electronics and sensing device applications. Significant changes occur in the

Raman spectrum of ATP when the junction switches from a high resistance (OFF) state to a low resistance (ON) state, which we attribute to a molecular change in ATP allows an Ag filament to form between the Ag NW and E2.

INTRODUCTION

There is tremendous interest in the field of molecular electronics as it has the potential to overcome size limitations associated with current silicon technology.¹⁹⁶ Accordingly, several groups have fabricated metal/molecule/metal junctions by various strategies in order to study the electronic properties of individual or small groups of molecules.^{63,69,76,158,197} While these studies have elegantly allowed for the conductance measurements of single molecules and provided new information about the electronic properties of molecules, most of the techniques suffer in that they are irreproducible, have low throughput, have a low success rate, and they are usually impractical for true device applications. In addition, many of the techniques only offer the ability to measure the electronic properties of the junction, rendering it difficult to understand the molecular processes leading to the interesting electronic properties, such as current rectification,¹⁵⁸ conductance switching,¹⁹⁷ and negative differential resistance (NDR).¹⁵⁵ Different vibrational spectroscopic techniques such as inelastic tunneling spectroscopy (IETS)¹⁹⁸, attenuated total internal reflection infrared spectroscopy¹⁹⁹ and surface-enhanced Raman spectroscopy (SERS)^{143-144,183,200-201} offer the ability to characterize the structure of molecules in an electronic junction. SERS is especially useful for spectroscopic measurements at nanogap metal electrodes^{143,183,200} since the metal can enhance the Raman signal, leading to possible single molecule sensitivity.

There are few examples of simultaneous measurements of conductance and SERS at different molecular junctions.¹⁴⁰⁻¹⁴² This strategy is very powerful for correlating changes in the electronic properties with the molecular structure in order to elucidate the mechanism of conductance. McCreery and co-workers fabricated nitroazobenzene molecular junctions using carbon as a substrate and were the first to report potential dependent spectral changes. They determined that the TiO_x layer contributed most to the observed conductivity changes in these junctions; the organic layer played a minor role but it was necessary to modulate TiO_x conductivity as it acted as a source of electrons. More recently, Natelson *et al.* and Yoon *et al.* demonstrated the use of nanoscale metal gap structures and crossed-nanowire molecular junctions, respectively, as a platform for simultaneous measurements of electronic conduction and Raman spectra.¹⁴³⁻¹⁴⁴

We recently described the electrochemical fabrication of Au (E1)/Ag NW/molecule/Au (E2) junctions, showing that our procedure is simple, fast, highly parallel, amenable to different molecules and thin films, and can be applied to sensing applications.¹⁹⁵ We also showed that the Ag NW contact can enhance the Raman scattering of molecules, such as aminothiophenol (ATP), in the junction (Chapter VI). Here we demonstrate that the AgNW contact can be used to enhance the Raman signal of ATP molecules in the junction while simultaneously monitoring the electronic properties of the junction.

EXPERIMENTAL SECTION

Electrode wiring and cleaning procedure. Refer to Chapter 2. section 2.2.2. for details.

Fabrication of Electrode/AgNW/ATP/Electrode junctions.

Electrode/AgNW/ATP/Electrode junctions were fabricated using the procedure as reported in Chapters II and VI.¹⁹⁵

RESULTS AND DISCUSSION

Figure 7.1A shows a schematic representation of the E1/Ag NW/ATP/E2 junction. Figure 7.1B shows an SEM image of one particular E1/Ag NW/ATP/E2 junction. ATP was chemisorbed on electrode 2 (E2) and Ag was electrodeposited on E1. Ag grew in the form of wires at E1 and made contact to E2, leading to the formation of an E1/Ag NW/ATP/E2 junction. Figure 7.1C shows the SERS spectrum of the ATP molecules obtained from the region represented by the red open circle in Figure 7.1B. We observed similar Raman modes for the ATP molecule as reported previously.¹⁹³

Table 7.1 shows the currents at -1V displayed by different devices. In comparison, the current for an Au-S-phenyl-S-Au (a similar molecule) junction based on single molecule resistance values reported in the literature ranges from 5.0×10^{-8} A ($R=20$ M Ω)- 4.8×10^{-7} A ($R=2$ M Ω).²⁰² 70% of our devices displayed currents that were 1 to 2 orders of magnitude lower than that reported in the literature. A few were larger (10^{-5} A) and two were in the range. The higher resistance could be due to a poor contact, or because there is an Ag/NH₂-phenol-S/Au contact instead of Au-S contacts at each end. The large values could be due to partial penetration of the Ag NW contact into the ATP SAM.

Figure 7.2A shows an i-V curve of an E1/Ag NW/ATP/E2 junction scanned from 0 to -1 to 1 and back to -1V at a scan rate of 100 mV/s (The potential sign is at the Au electrode). The current passing through the device was 2.2×10^{-8} A and the i-V curve is ohmic with some hysteresis at -1V ($R=45$ M Ω). In order to test if the junction would switch from a low conductance to high conductance state the potential was scanned from

Figure 7.1. A) Illustration of E1/Ag NW/ATP/E2 junction (B) SEM image showing E1/Ag NW/ATP/E2 junction. Red open circle represents the region from which SERS spectra were obtained and (C) SERS spectra (632.8 nm laser) of ATP molecules obtained from the region represented by red open circle in frame B.

Table 7.1. Currents displayed by different devices with E1/Ag NW/ATP/E2 junctions at -1V.

Sample	Current (A)
1	1.07×10^{-9}
2	0.70×10^{-8}
3	1.12×10^{-10}
4	0.92×10^{-9}
5	1.92×10^{-10}
6	3.23×10^{-10}
7	4.53×10^{-9}
8	0.02×10^{-3}
9	3.02×10^{-11}
10	0.01×10^{-3}
11	3.46×10^{-8}
12	0.56×10^{-9}
13	0.13×10^{-7}

Figure 7.2. A) i-V plot of an E1/AgNW/ATP/E2 junction from A) -1 V to 1 V (Background with no Ag NW or ATP also shown) and B) -5 V to 5 V. C) i-V plot of E1/AgNW/ATP/E2 junction from different device from -1 V to 1 V (Background with no Ag NW or ATP also shown) and D) -5 V to 5 V.

5 to -5 V. Figure 7.2B shows the i-V curve of the same device from 5 to -5 V collected by sweeping the potential from 0 to -5 to 5 and back to 0V as indicated by the black arrows, showing mostly ohmic behavior again with slight hysteresis. Figure 7.2C shows an i-V curve of a different higher resistance E1/Ag NW/ATP/E2 junction scanned from 0 to -1 to 1 and back to -1V at a scan rate of 100mV/s. The current passing through the device was 1.3×10^{-10} A ($R=7692 \text{ M}\Omega$) at -1V. Figure 7.2D shows the i-V curve of the same device from 5 to -5V collected by sweeping the potential from 0 to -5 to 5 and back to 0V as indicated by the black arrows. In this case the junction switched from a low current state to a high current state once the applied potential was more negative than -3 V and remained in the high current state until the applied potential was more positive than -2V on the return scan (see Figure 7.2D). The current remained low at positive voltages, showing diode-like behavior. Figure 7.3 shows i-t plots of an E1/Ag NW/ATP/E2 junction when the potential was stepped between 0.1V and +3V, -2V, -3V and -6V respectively. The current increased three orders of magnitude once the applied potential was more negative than -3V, increased less at -2V, and did not increase significantly at +3V.

E1/Ag NW/ATP/E2 junctions whose currents were in the 10^{-8} A range at -1 V exhibited ohmic behavior with little hysteresis and no conductance switching, whereas E1/Ag NW/ATP/E2 junctions whose currents were in the 10^{-10} A range at -1 V exhibited conductance switching at more negative potentials. Since the high resistance devices exhibited switching behavior, we decided to correlate the electronic properties of these junctions with the Raman spectrum of ATP. In order to correlate the electronic properties (switching behavior) of the junction with the ATP structural properties, we

Figure 7.3. Current-time plots of the E1/Ag NW/ATP/E2 junction when the applied potential was stepped between A) 0.1V to +3V and held at +3V for 70 s, B) 0.1V to -2V, C) 0.1V to -3V and D) 0.1V to -6V with a holding time of 10 s at each potential. There is a three order of magnitude change in current when the applied potential is more negative than -3V.

obtained SERS spectra and i-t plots simultaneously while the potential was stepped between 0.1V (current off) and -3 V (current on) with a 10 s holding time at each potential. Figure 7.4A shows an i-t plot of the junction while the voltage was stepped between 0.1V and -3V. The molecule reversibly switched from a low current state to a high current state with a potential change from 0.1 to -3 V. There was also a great deal of current fluctuations in the “on” state. The current increased three orders of magnitude from $\sim 3.6 \times 10^{-10}$ to $\sim 1.5 \times 10^{-7}$ A when the potential was switched from 0.1 V to -3 V (Figure 7.4A).

Figure 7.4B shows SERS spectra recorded while we altered the potential applied across the junction between 0.1 and -3 V. The spectrum at 0.1V (Figure 7.4Ba) is similar to the spectrum obtained when there was no external electric field applied (Figure 7.1B). The spectrum at -3 V (Figure 7.4Bb) (current on) displayed a significant increase in intensity of the peak at 1587 cm^{-1} (CC str in phenyl ring and NH_2 bend) while the peaks at 1139 cm^{-1} (CH bend), 1389 cm^{-1} (CC str in phenyl ring and CH rock and NH_2 rock) and 1434 cm^{-1} (CC str in phenyl ring and NH_2 rock) disappeared. There was a small decrease in the S-C mode at 1084 cm^{-1} at -3 V, but its presence indicates that the -S-C bond remained intact during the conductance change. The peaks at 1139 , 1389 and 1434 cm^{-1} reappeared and the intensity of the peak at 1587 cm^{-1} decreased again at a 0.1 V (Figure 7.4Bc), showing reversibility in the conductivity and SERS data. Natelson *et al* also correlated the Raman spectra of ATP and the conductance, but the Raman data focused on correlated fluctuations between the Raman spectrum and conductance at a constant voltage.¹⁴³ With an increase in conductance, they observed both an increase and decrease in the intensity of a Raman band at 1522 cm^{-1} at different times.

Figure 7.4. A) i-t plot of the device with E1/Ag NW/ATP/E2 junction when the potential was stepped between 0.1 and -3V and (B) SERS spectra of ATP molecules collected from an E1/Ag NW/ATP/E2 junction of the same device while the potential was stepped for 10 s between -3 V (a and c) and 0.1 V (b and d) as indicated.

There are multiple E1/Ag NW/ATP/E2 junctions in each device. For devices with switching behavior, we tested the Raman as a function of potential for all the junctions. Figure 7.5 shows the results of 3 other junctions separate from that shown in Figure 7.4. Two of those (A and B) junctions showed no significant change at -3V. The third junction (frame C) showed the emergence of a broad peak near 1300 cm^{-1} and a decrease in the other bands. Figure 7.5 D shows the ATP SAM away from the Ag NW at 0.1 V and -3V. The signal is low and the spectrum changed minimally. In junctions that did not display a significant Raman change, the Ag NW contact was likely not in close enough contact to contribute significantly to the conductivity of the entire device, but was close enough to give some Raman enhancement. We discussed the correlation between Raman enhancement and device current in Chapter VI.

Several mechanisms, such as oxidation/reduction of molecules, rotation of molecular backbones, rotation of functional groups, interaction with neighboring molecules, fluctuation of bonds, and change of metal molecule hybridization have been proposed to be responsible for the switching behavior in molecules.²⁰² Filament formation through molecular monolayers at Ag electrodes has also been shown as a conductance switching mechanism.²⁰³ In order to test if the conductance switching property was inherent to the ATP molecule or due to possible Ag filament formation through the monolayer, we fabricated devices with hexanethiol in the junction and measured the electronic properties (Figure 7.6). E1/Ag NW/hexanethiol/E2 junctions displayed similar electronic properties as that of E1/Ag NW/ATP/E2 junctions. E1/Ag NW/hexanethiol/E2 junctions whose currents are in the 10^{-10} A range at -1 V exhibited conductance switching and those with currents in the 10^{-8} range at -1 V displayed ohmic behavior. Figure 7.6A and 7.6C show

Figure 7.5. A-C) SERS spectra of ATP obtained from different E1/Ag NW/ATP/E2 junctions when the applied potential was 0.1 and -3V. The red spectra were obtained when the applied potential was 0.1 V and black spectra obtained when the potential was -3V. Figures A and B represent the SERS spectra collected from E1/Ag NW/ATP/E2 junctions which did not show significant changes in the spectrum at -3V. D) SERS spectra obtained from the surface of the electrode E2 where ATP was chemisorbed at 0.1V was applied (Black spectrum) and when -3V was applied (Red spectrum).

Figure 7.6. A) i-V plot of an E1/AgNW/Hexanethiol/E2 junction from A) -1 V to 1 V (Background with no Ag NW or ATP also shown) and B) -5 V to 5 V. C) i-V plot of E1/AgNW/Hexanethiol/E2 junction from different device from -1 V to 1 V (Background with no Ag NW or ATP also shown) and D) -5 V to 5 V.

i-V curves scanned from 0 to -1 to 1 and back to -1 V at a scan rate of 100 mV/s for E1/Ag NW/hexanethiol/E2 junctions whose currents are in the 10^{-10} and 10^{-8} A range, respectively. Figure 7.6B and 7.6D show i-V curves of these devices from 5 to -5 V collected by sweeping the potential from 0 to -5 to 5 and back to 0 V as indicated by the black arrows. Conductance switching clearly occurred near -3 V for high resistance these junctions with hexanethiol as well as ATP. Conductance switching also occurred near -3 V in devices where there was no molecule in the junction (bare nanogap electrode devices) as described in Chapter V.

Low conductance E1/Ag NW/SAM/E2 junctions, where the SAM is hexanethiol or ATP, and bare nanogap electrodes both exhibited conductance switching properties near -3 V. Accordingly, we conclude that the conductance switching is not specific to the ATP molecules. It is a general property, which is more consistent with the conductance switching via Ag filament formation through the monolayer. It is important to note that there are some notable differences between the switching properties of SAM junctions (ATP and hexanethiol) compared to bare Ag/air junctions. First, the SAM junctions displayed currents ~ 2 orders of magnitude lower at -5 V as compared to the bare nanogap electrodes. Second, the SAM exhibited more diode like behavior (greater difference between the currents at + and - potentials) as compared to nanogap electrodes. Finally, the SAM junctions exhibited a sharp current increase when switching on, while bare nanogap junctions showed a more gradual current increase that began at less negative voltages. These observations suggest that the presence of the SAM hinders Ag filament formation at negative voltages and prevents it completely at positive voltages.

The Raman spectrum for ATP was significantly different in the high conductance

state compared to the low conductance state, even though the conductance change appears to be a consequence of Ag filament formation. From these differences, it appears that the presence of a SAM hinders the filament formation process, leading to a more negative threshold voltages with an abrupt current change instead of gradual filament formation at less negative voltage for the bare junctions. The lack of switching for lower resistance junctions (10^{-8} A) can be explained by the fact that a stable Ag filament likely formed during electrochemical fabrication and was already present, leading to higher current and no switching since it was already “on”.

We believe that a structural or chemical change takes place in the ATP that allows the filament to form and penetrate the SAM. This is consistent with a change in the Raman of ATP that correlates with a filament based conductance change. More work is required to confirm this and understand the details of the change in ATP.

CONCLUSIONS

In summary, we demonstrated simultaneous conductivity and SERS measurements at electrochemically-fabricated E1/Ag NW/ATP/E2 junctions. Our data showed a change in the ATP SAM (chemical or structural) that correlated with filament formation. The filament formation at SAM junctions was also distinctly different from bare metal nanogap junctions. Future studies will explore the effect of different SAM molecules on filament formation, a study of the ATP Raman spectrum over the entire ± 5 V range, and the lack of switching behavior for low resistance conductance junctions. We will also test the combined system with molecules that have well known electronic switching properties not based on filament formation. Although the conductance switching was due

to Ag filament formation in this case, we believe our results demonstrate the the power of our system for performing this system is very powerful for performing simultaneous conductivity and SERS measurements at molecular junctions to better understand the electronic properties of molecules.

CHAPTER VIII

SUMMARY AND CONCLUSIONS

This thesis has described an electrochemical approach for fabricating metal/metal and metal/molecule/metal junctions at micron gap gold electrodes. The approach is simple, fast, highly parallel, and can be applied to fabricate a wide variety of electronic nano devices with potential applications in nanoelectronics, molecular electronics, and chemiresistive sensing.

We successfully fabricated the following nanoscale junctions combining electrochemistry and self assembly: (Electrode 1, Electrode 2 and nanowire are abbreviated as E1, E2, NW, respectively)

- 1) E1/nano Pd/E2 junctions
- 2) E1/nano Pd/polyphenol/E2 junctions
- 3) E1/Ag NW/E2 junctions
- 4) E1/Ag NW/polyphenol/E2 junctions
- 5) E1/Ag NW/SAM (butanethiol, hexanethiol, dodecanethiol, octadecanethiol, and aminothiophenol)/E2 junctions.

Pd deposits were dendritic or flower-like micro/nano structures whereas Ag deposited in the form of wires (or needles) across the 5 micron gap Au electrodes. In one procedure, the junction resistance was controlled by electrodepositing polyphenol of different densities within the junction. This procedure did not lead to precise control over the resistance, but the number of polyphenol cycles did offer some general resistance

control over 9 orders of magnitude. We also controlled the junction resistance by assembling SAMs of different chain lengths within the junction. While the resistance was not precisely controlled, the % of shorts from the nano metal through the SAM decreased as the chain length of the SAM increased. The H₂ sensing properties of E1/nano Pd/E2, E1/nano Pd/polyphenol/E2 and E1/AgNW/polyphenol/E2 junctions functionalized with Pd nanoparticles for H₂ sensing were explored. The following are conclusions drawn from those studies.

- E1/nano Pd/E2 junctions displayed currents on the mA level at -0.3V and exhibited fast and reversible decreases in current in the presence of H₂ concentrations in a N₂ carrier gas with an average detection limit of 400 ppm. The current decrease was due to the formation of more resistive PdH_x relative to Pd in the presence of H₂.
- E1/nano Pd/polyphenol/E2 junctions exhibited currents in the range of 10-100 pA at -0.3V and displayed a 6-7 order of magnitude increase in current for concentrations above 1.0% H₂. The increase in current was due to volume expansion upon PdH_x formation, which led to a direct contact between Pd as (PdH_x) and E2 through the porous 4 -10 nm thick polyphenol insulating film.
- High resistance E1/Ag NW/polyphenol/E2 junctions functionalized with Pd nanoparticles responded fast and reversibly to H₂ concentrations as low as 0.11% (1100 ppm) in a nitrogen carrier gas by a resistance decrease, likely due to volume expansion of the Pd nanoparticles.

We studied the enhancement of Raman scattering signals of ATP molecules in electrochemically fabricated E1/Ag NW/ATP/E2 junctions. The following are the conclusions drawn from that study:

- The presence of the Ag nanowire at the junction led to strong Raman scattering of the molecules within the nanojunction leading to enhancement factors estimated as high as 10^6 - 10^8 . The Ag NW acted similarly to a tip in Tip Enhanced Raman Spectroscopy (TERS), except in a planar chip format.
- The SERS enhancement at several junctions within a device allowed us to determine the extent of contact between the Ag NW and ATP SAM.
- Submonolayer coverages of SAMs within the junction, specifically ATP molecules diluted by 1000 with hexanethiol molecules, within the junction could be detected by SERS with the Ag NW contact. We roughly estimate approximately 5 molecules in the junction at this concentration.

Electrochemically fabricated metal/organic/metal junctions were used as a platform for measuring the conductivity and SERS of E1/Ag NW/ATP/electrode junctions simultaneously. The conclusions from this study are as follows:

- 70% of E1/Ag NW/ATP/E2 junctions displayed currents that were 1 to 2 orders of magnitude lower than reported in the literature for Au-S-phenyl-S-Au junctions. This could be partly due to weak and different nature of the contact.
- E1/Ag NW/ATP/electrode junctions with currents near 10^{-8} A at -1V exhibited ohmic behavior and no filament switching behavior up to ± 5 V, likely because a stable Ag filament already formed.

- E1/Ag NW/ATP/E2 junctions with currents near 10^{-10} A at -1V exhibited conductance switching behavior based on Ag filament formation.
- Junctions with hexanethiol exhibited similar switching behavior as those with ATP and bare junctions, consistent with Ag filament based switching.
- E1/Ag NW/ATP/E2 junctions with high resistance switched from a low current state to high current state once the applied potential was more negative than -3V and remained in the high current state until the applied potential was more positive than -2V on the return scan. The current increased by three orders of magnitude when the potential was switched from 0.1V to -3V.
- E1/Ag NW/ATP junctions with high resistance were used for correlating the electronic properties of the junction to the chemical and structural properties of ATP.
- Significant changes in the Raman modes were observed when the potential was switched from 0.1V to -3V. Certain Raman modes showed an increase in intensity while others decreased with an increase in conductance. The conductivity and SERS data were reversible when the potential was switched between -3V and 0.1V. While ATP was not directly responsible for the switching behavior, we believe it undergoes Raman sensitive changes that allow Ag filament formation to occur.
- Nanogap electrodes fabricated between Ag NWs and an Au electrode also also exhibited filament-based conductance switching when the applied potential was more negative than -3V.

- Molecule-based (ATP and hexanethiol) devices behaved as bipolar resistance switches whereas nanogap devices without a molecule in the gap behaved as unipolar resistance switches.
- The changes in the electronic properties of the junctions occurred due to Ag filament formation at a bare electrode gap or through the monolayers.
- The observed Raman changes for ATP in the high and low conductance state was likely due to chemical or structural changes that make Ag filament formation possible.

Finally, the resistance switches formed by electrochemically fabricating nanogaps between Ag NWs and an Au electrode exhibited on/off ratios over 10^4 and long endurance (at least 10^2 cycles). This offers promise for use as a memory device.

This dissertation demonstrates that the combination of electrochemistry, self-assembly, and microfabrication is a powerful tool for the simple, rapid fabrication of working electronic or sensing nanodevices on a bench top at low cost with the ability to utilize SERS characterization. Improvement is still needed in the isolation of single NWs, decreasing the size of contacts, increasing the density of the devices, and improving reproducibility. The work described here lays down the foundation for several exciting future studies to be explored.

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APPENDIX

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Electrochemical Fabrication of Metal/Organic/Metal Junctions for Molecular Electronics and Sensing Applications

Author: Radhika Dasari et al.

Publication: Langmuir

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EDUCATIONAL BACKGROUND:

University of Louisville (Louisville, KY)

Ph.D in chemistry, expected August 2011

2005-present

Department of Chemistry (Dr. Francis P. Zamborini)

Dissertation Title: “Electrochemical Fabrication of Nanoscale Molecular Junctions: Surface-enhanced Raman Spectroscopy Characterization, Sensing, and Molecular Electronics Applications”

Kakatiya University (Warangal, India)

Bachelors in Pharmacy

2000-2004

RESEARCH EXPERIENCE:

University of Louisville (Louisville, KY)

2005-present

Graduate Research Assistant: Fabricated metal based and molecule based electronic devices by an electrochemical method for molecular electronics and sensing applications. This involved combining metal electrodeposition with electropolymerization or self assembly of monolayers. I used polymer based junctions for sensing H₂ and molecule-based junctions for correlating the electronic switching properties of aminothiophenol (ATP) with the spectroscopy of the ATP determined by SERS at the junction. I developed a simple approach for fabricating polymer and molecule based electronic devices and demonstrated sensing behavior and combined spectroscopic and electronic measurements.

RESEARCH JOURNAL PUBLICATIONS:

- 1 Dasari, R.; Zamborini, F. P. “Electrochemical Fabrication of Nanoscale Two-Terminal Resistive Switching Devices” (Manuscript in preparation)

- 2 Dasari, R.; Zamborini, F. P. "Tip Enhanced Raman Spectroscopy on Planar Surfaces" (Manuscript in preparation)
- 3 Dasari, R.; Zamborini, F. P. "Simultaneous Conductivity and Enhanced Raman Spectroscopy Measurements at Electrochemically-Fabricated Metal/Organic/Metal Junctions" (Manuscript in preparation)
- 4 Dasari, R.; Ibañez, F. J.; Zamborini, F. P. "Electrochemical Fabrication of Metal/Organic/Metal Junctions for Molecular Electronics and Sensing Applications" *Langmuir* **2010** ASAP article. This work is highlighted on the journals cover page in the June 7, 2011 issue.
- 5 Dasari, R.; Zamborini F. P.; "Hydrogen Switches and Sensors Fabricated by Combining Electropolymerization and Pd Electrodeposition at Microgap Electrodes" *J. Am. Chem. Soc.* **2008**, 130, 16138-16139.

PATENTS:

- 1 Dasari, R.; Zamborini, F. P.; "Sensors and Switches for Detecting Hydrogen" Patent Number - US 20100108529

PRESENTATIONS:

- 1 **Radhika Dasari** and Francis P. Zamborini. *Simultaneous Conductivity and Enhanced Raman Spectroscopy Measurements at Electrochemically Fabricated Metal-Organic-Metal Nanojunctions*. **Central Regional Meeting of the American Chemical Society**, Indianapolis, IN June 08-10, 2011 – Poster Presentation.
- 2 **Maune, M. A.**; Dasari, R.; Beeram, S. R.; Zamborini, F. P. *Selective Edge Attachment of Antibodies and Gold Nanospheres for Improved Localized Surface Plasmon Resonance (LSPR) Sensing and Enhanced Raman Scattering Spectroscopy*. **Undergraduate Research Symposium**, Louisville, KY, April 19, 2011 – Poster Presentation.
- 3 **Maune, M. A.**; Dasari, R.; Beeram, S. R.; Zamborini, F. P. *Selective Edge Attachment of Antibodies and Gold Nanospheres for Improved Localized Surface Plasmon Resonance (LSPR) Sensing and Enhanced Raman Scattering Spectroscopy*. **University of Kentucky Undergraduate Research Symposium**, Lexington, KY, April 15, 2011 – Poster Presentation.
- 4 **Radhika Dasari** and Francis P. Zamborini. *Electrochemical Fabrication of Metal/Organic/Metal Junctions for Molecular Electronics or Sensing Applications*. **Electrochemistry Mini Symposium sponsored by the Cleveland section of the Electrochemical Society and the Yeager Center**

- for Electrochemical Sciences**, Case Western Reserve University, Cleveland, Ohio, May, 2010 - Poster Presentation.
- 5 **Radhika Dasari** and Francis P. Zamborini. *Electrochemical Approach for Fabricating Devices for Sensing or Molecular Electronics Applications*. **University of Louisville Graduate Research Symposium**, Louisville, KY, USA, Mar 6, 2010 - Poster Presentation.
 - 6 **Radhika Dasari** and Francis P. Zamborini. *Electrochemical Approach for Fabricating Devices for Sensing or Molecular Electronics Applications*. **Pittcon**, Orlando, FL, USA, Feb 28-Mar 5, 2010 - Poster Presentation.
 - 7 **Radhika Dasari** and Francis P. Zamborini. *Electrochemical Approach for Fabricating Devices for Sensing and Molecular Electronics Applications*. **Central Regional Meeting of the American Chemical Society**, Cleveland, OH, USA, May 20-23, 2009 - Oral Presentation.
 - 8 **Radhika Dasari** and Francis P. Zamborini. *Electrochemical Method for Fabricating Metal/Molecule/Metal Junctions and their Sensing Applications*. **Fifth Kentucky and Entrepreneurship Conference**, Louisville, KY, USA, April 7, 2009 - Poster Presentation.
 - 9 **Radhika Dasari** and Francis P. Zamborini. *Electrochemical Method for Fabricating Metal/Molecule/Metal junctions and their Sensing Applications*. **Pittcon**, Chicago, IL, USA, March 7-13, 2009 - Poster Presentation.
 - 10 **Radhika Dasari** and Francis P. Zamborini. *Electrochemical Method for Fabricating Metal/Molecule/Metal junctions and their Sensing Applications*. **University of Louisville 1st Graduate Research Symposium**, Louisville, KY, USA, March 6, 2009 - Poster Presentation.
 - 11 **Radhika Dasari** and Francis P. Zamborini. *Electrochemical Deposition of Silver and Palladium Nanostructures at Microgap Electrodes for Sensing Applications*. **KY Nanomat**, Louisville, KY, USA, March 16-18, 2007 - Poster Presentation.

INSTRUMENTATION:

- Electrochemistry- Cyclic Voltammetry, Chronocoulometry and Chronoamperometry
- Microscopic Techniques – Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM)
- Spectroscopy Techniques – UV-vis, Raman and Atomic Absorption Spectroscopy (AAS)

- Separation Techniques – Gas Chromatography (GC)

TEACHING EXPERIENCE:

- Graduate Teaching Assistant Fall 2005 – Fall 2009
Proctored and graded for General Chemistry 201/202 and 101.

Lectured, supervised and graded pre-labs and lab reports for Introduction to Chemical Analysis I, II, III and IV.
- High School Student Research Mentor Fall 2009
Trained 2 students in laboratory techniques, designed experiments and assisted with the preparation of a poster presentation.
- Undergraduate Research Mentor Fall 2010 and Spring 2011
Taught basic laboratory techniques, instrumentation, basic concepts of chemistry, and synthesis and characterization of metal nanostructures. Helped the students prepare oral presentations for group meetings and poster for poster presentation.
- Graduate Research Mentor:
Taught basic laboratory techniques, instrumentation, synthesis of metal nanostructures and characterization.

AWARDS:

- Excellence in safety in the teaching laboratory.
- Travel award from Graduate Student Council (GSC) for Pittcon 2009, Pittcon 2010 and Central Regional Meeting of the American Chemical Society 2009.

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