

PREPARATION OF QUANTUM FINGERPRINT™-READY  
METAL-GALLIUM ARSENIDE INTERFACES FOR  
MOLECULAR CHARACTERIZATION

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Master of Science

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by

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The undersigned, appointed by the Dean of the Graduate School, have examined the thesis entitled

PREPARATION OF QUANTUM FINGERPRINT™-READY METAL-GALLIUM  
ARSENIDE INTERFACES FOR MOLECULAR CHARACTERIZATION

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## **ABSTRACT**

Quantum Fingerprint™ (Charge Based Transient Level Spectroscopy Analysis) trace chemical detectors are desirable due to their high sensitivity, high selectivity, rapid acquisition and response rates, and robustness. These detectors are able to detect trace amounts of the target species (less than ppb denominations). High sensitivity is a desired feature in the field; most situations call for foreign environments and samples of mixed species. The detector's ability to function with minimum delays allows for rapid sampling and data processing. Quantum Fingerprint™ detectors are promising due to its long operating life, low maintenance costs, and resilience to rugged environments.

Undoped Gallium Arsenide served as the base material for the Quantum Fingerprint™ sensor's metal-semiconductor interface. This report elaborates on the importance of Ohmic and Schottky contacts for the viability of a semiconductor-based device and the preparation of metal-semiconductor interfaces. The interface is centered on a Gallium Arsenide (1 cm x 1 cm) square wafer. A (Nickel/ Germanium/ Gold/ Nickel/ Gold/ Nickel) deposition is placed on one side of the Gallium Arsenide Wafer. The other side of the interface is undoped Gallium Arsenide. Gallium Arsenide served as a viable semiconductor base material, since water vapor was detected in both open-air and deionized water modules

## I. INTRODUCTION

Metallization systems are critical in creating semiconductor devices and integrated circuits. The metallization systems serve as the electrical junction between the semiconductor's active region and the external circuit. Metallizations can transport current densities of over 10 Amperes per cm<sup>2</sup>. The excessive current density leads to electromigration. During electromigration, the electrons induce atoms to move in the direction of electron flow. Electromigration does not overpower at interconnections of integrated circuits and regions of high current density [1].

Optimal contacts are defined by the following characteristics: the contacts need to exhibit the correct electrical behavior, the contacts must display proper stability during operation, the contacts should be resilient to metallurgical reactions, and the contacts should accommodate the possibility of selective etchability between the metal film and Gallium Arsenide. The contacts should adhere well to the Gallium Arsenide surface and accommodate wire bonding [1].

A barrier, against electron and hole flow, is made when metals are deposited upon the semiconductor. The barrier is expressed by the following equation.

$$\Phi_{bn} = \Phi_m - \chi_{sc} \quad \text{Eq. 1}$$

$\Phi_{bn}$  refers to electron barrier height,  $\Phi_m$  refers to metal work function, and  $\chi_{sc}$  refers to semiconductor electron affinity.

Hole barrier height is expressed by the following equation:

$$\Phi_{bp} = (E_g/q) - (\Phi_m - \chi_{sc}) \quad \text{Eq 2}$$

$\Phi_{bp}$  refers to hole barrier height,  $E_g$  refers to the band gap of the semiconductor, and  $q$  denotes the electronic charge.

For n-type semiconductors, ideal Ohmic contacts are obtained when the metal work function is less than or equal to the semiconductor's electron affinity. Ohmic contacts are ensured when the electron barrier height is less than or equal to zero. Ideal Schottky barriers are observed in n-type semiconductors when the following conditions are met: the metal work function is greater than the semiconductor's electron affinity and the electron barrier height is greater than zero [1].

In a regular setting, the aforementioned cases are not observed. The barrier height for metal/ Gallium Arsenide systems is independent of the metal work function. The behavior of barriers is influenced by Fermi level pinning at the semiconductor surface. The pinning happens due to the submonolayer coverages of different metals and oxygen. During pinning, charge is redistributed between the metal and the semiconductor surface. Fermi level pinning occurs when the surface state density is  $10^{13}$  per  $\text{cm}^2$  or more. The metal and the semiconductor surface will then reach thermal equilibrium. The Fermi level will then equalize. The pinning level will be independent of contamination. Pinning will occur 0.8 eV below the conduction band minimum. This process serves as a precursor to the Unified Defect Model. In the Unified Defect Model, each surface state are associated with the native defects of the acceptor or donor [1]. This model can applied to Schottky barriers adhered to compound semiconductors

Quantum Fingerprint™ devices require both Ohmic and Schottky contacts. Ohmic contacts ensure that little resistance is introduced to the metal/ semiconductor interface [1]. The limited resistance, that enters the metal/ semiconductor interface, is negligible when the semiconductor device is used. Schottky barriers serve as diodes. Schottky barriers can convert alternating current into direct current. Schottky barriers is characterized by the

electrical properties of its reacted and inter-diffused regions of the metal-semiconductor interface. The Quantum Fingerprint™ requires that one contact be an Ohmic contact and the other be a Schottky Barrier.

## II. PREVIOUS TRIALS

Table 2

### CONVENTIONAL PROTOCOL FOR QUANTUM FINGERPRINT™ SENSOR CHIP DEVELOPMENT [2]

CLEANING PHASE	PROCESSES
Cleaning	Acetone → Methanol → Deionized Water
Material Characterization	FTIR, RAMAN, SEM, & EDS
Electrical Characterization	I-V Test, Sheet Resistance, Bulk Resistivity
Cleaning	Piranha → Hydrofluoric Acid → RCA-1 → RCA-2 → IPA → Acetone
Cleaning	Plasma Cleaning (5% H <sub>2</sub> , 95% Ar)
Metallization	Sputtered metals include: Au, Al, Ni, Pt, Ti
Annealing	Annealed in H <sub>2</sub> or Ar atmospheres
Electrical Characterization	I-V Measurement
Quantum Fingerprint™ Measurement	Raw Data Collection & Signal Analysis

### KEY ASPECTS OF CONVENTIONAL SENSOR CHIP DEVELOPMENT

#### A. MATERIAL CHARACTERIZATION

Material characterization is essential in determining the substrate's material composition and topography. Characterization processes include Raman Spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Electron Dispersive Spectroscopy.

Both Raman and Infrared Spectroscopy data is derived from the measurement of changes in molecular vibrations between the substrate's atoms. The oscillation between molecules are defined by the following relationship [2]:

$$E_{vb} = hv_0 \left[ \left( n + \frac{1}{2} \right) - x_a \left( n + \frac{1}{2} \right)^2 \right]. \quad \text{Eq 3}$$

$E_{vb}$  represents vibrational energy,  $h$  represents Planck's constant,  $v_0$  represents the vibrational frequency,  $n$  represents the vibrational quantum number, and  $x_a$  represents the anharmonicity constant. Infrared spectroscopy measurements are made in modes of absorption, transmission, and the reflection of incident infrared beams. When a molecule transitions from its ground state to its excited state, infrared energy will be absorbed. The absorption of energy is shown by the substrate's change in wavelength.

Stokes Raman scattering focuses on the frequency of  $V_L$  (elastic Rayleigh scattering) –  $V_M$  (frequency of molecular vibration); this frequency is achieved when shifts occur from lower to higher vibrational energy levels. Rayleigh ( $V_L$ ) scattering indicates that the energy transitions begin and end at identical vibrational energy levels. The frequency of  $V_L + V_M$  (anti-Stokes Raman scattering) denotes the shift from higher to lower vibrational energy levels. As light strikes the sample molecule, chemical bonds represent the change in energy values [3].

Scanning Electron Microscopy (SEM) allows the user to obtain information about the substrate's elemental composition and surface topography. Scanning Electron Microscopy allows the user to examine substrates from nanometer to micron scales. As an electron beam is focused onto the specimen, the incident electrons' beam loses energy over a small area on the specimen. The interaction can penetrate into the specimen. The penetration depends on the specimen's atomic number and density, and the incident

electron's energy. The interaction between the incident electron beam and the specimen leads to the following by-products: secondary electrons, backscattered electrons, characteristic x-rays, and photons of various energies [2].

Cathode Ray Tubes (CRT), and other equipment, allow the user to document the prior interactions. Amplified signals are depicted as fluctuations in brightness by the Cathode Ray Tube. Raster Scanning (a CRT feature) across the substrate's surface resembles the electron beam interacting with the specimen. The intensity map, produced from the electron beam's interaction with the substrate, is portrayed on the CRT's display [4].

Electron Dispersive Spectroscopy serves as another mode for Scanning Electron Microscopy analysis. In this process, the substrate's inner electron shell electron is ionized, as the electron beam interacts with the specimen. This interaction creates auger electrons and substrate-characteristic x-rays. The following figure and spectra come from the analysis of the Silicon substrate. Each numerical annotation corresponds to a region on the substrate; an electron dispersive spectra will accompany each region [2].

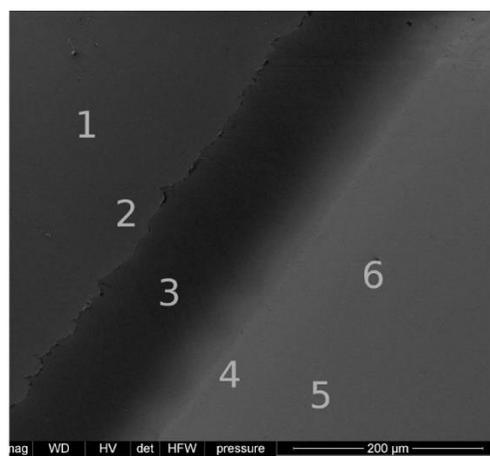
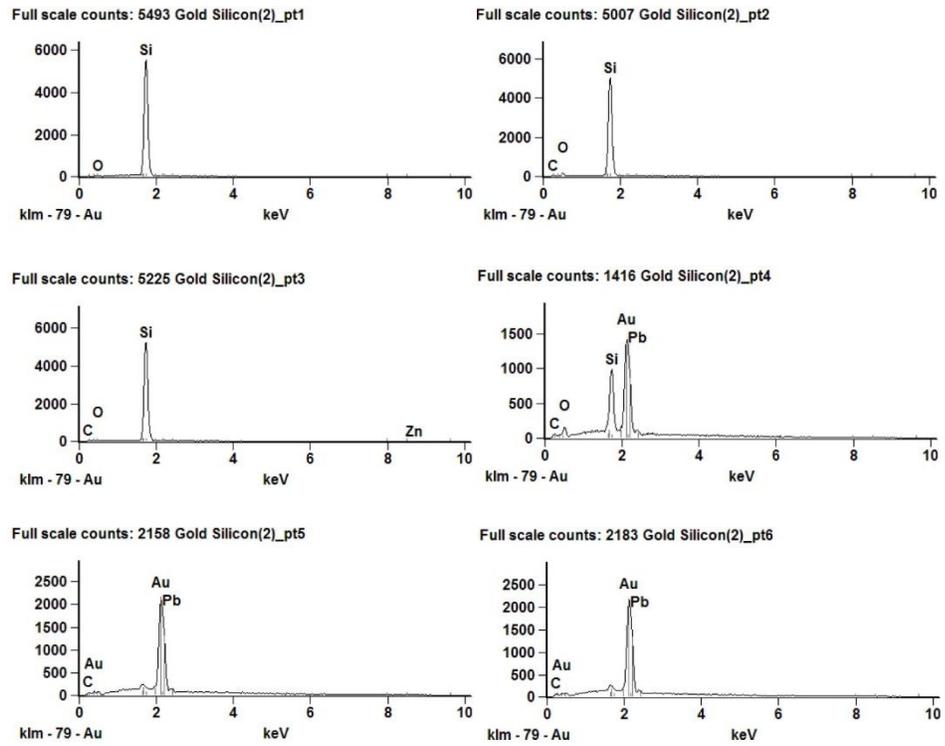


Figure A-1 SEM Spectra of Metallized Sensor Chips [2]

Figure A-2 EDS Spectra for Metallized Sensor Chips [2]



## **B. ELECTRICAL CHARACTERIZATION (BEFORE AND AFTER SENSOR CHIP PREPARATION)**

Each sensor chip possesses its own electrical signature; semiconductor contacts have varying resistance and capacitance values. The Ohmic contact on a sensor chip is analyzed by current-voltage (I-V test) measurements.

Current-voltage measurements are measured with an Agilent E5272A ammeter. The measurements are recorded onto the computer with the help of a Visual Basic computer code. Measurements, on the Ohmic contact, focus on the linearity and symmetrical response of current against voltage. These responses are observed at both forward and reverse biases [5].

Resistance is measured as two fine needles (two-point probe approach) are pressed onto the sensor chip's contacts. Through the two-point probe method, total resistance measurements are attained from the contact; the sum of the sheet resistance ( $R_{SH}$ ) and contact resistance ( $R_C$ ) provides the total resistance. Resistivity measurements can also be attained with four-point probes (Jandel Engineering RM3-AR) [2].

## **C. SUBSTRATE CLEANING**

Substrate contaminants compromise the integrity of the substrate and the resulting sensor chips. Contamination leads to untidy surfaces, changes in substrate surface [6] dimensions, irregularities in surface topography, and the sensor chip's overall viability.

The RCA (Radio Corporation of America) cleaning method was predominantly used to alleviate contaminants such as particles, chemicals, metallic ions, airborne particles, and bacteria. The RCA cleaning method aids in removing organic, oxide, and ionic layers. The cleaning method has been modified for Dr. Annie Yuning Hsu Tipton's

procedure in order to accommodate the following factors: small-scale laboratory manufacturing facilities and dilute solvents [2].

The following solvents are used for substrate cleaning [7]:

A. Caro's (Piranha) Acid (effective for organic residues)

- The mixture of Sulfuric Acid and Hydrogen Peroxide (ratios range from 2:1 to 4:1) acts as the solvent.
- The substrate will be boiled in the solvent for 10 to 15 minutes (130°C).
- The substrate will be rinsed in Deionized Water. The substrate will be subjected to an ultrasonic bath for five minutes to minimize residue.

B. Hydrofluoric (HF) Acid

- The mixture of Hydrofluoric Acid and Deionized Water (Ratio of 1:50) acts as the solvent. The HF solvent aids in removing the top oxide layer.
- The substrate is immersed in the Hydrofluoric Acid solution at room temperature. A hydrophilic substrate surface is observed while the substrate is submerged in the fluid; the surface then becomes hydrophobic as the substrate is taken out. The substrate's surface demonstrates strong hydrophobicity 15 seconds after removal.

C. RCA Standard Clean-1 (RCA SC-1)

- Alkaline Peroxide Mixture: Deionized Water, Hydrogen Peroxide, and Ammonium Hydroxide (Ratios range from 5:1:1 to 50:1:1). As the mixture becomes more diluted, safety is ensured, the occurrence of micro-roughing lessens, manufacturing costs become lower, and the whole cleaning procedure becomes more fluid.

- This mixture removes organic surface films and metals. The metals include Aluminum, Gold, Copper, Nickel, Cadmium, Zinc, Cobalt, and Chromium.
- The chemical mixture is heated to about 75 to 80°C. The substrate will be simmered in the mixture for five minutes.
- The substrate will be rinsed in Deionized Water. The substrate will be subjected to an ultrasonic bath for five minutes to minimize residue.

#### D. RCA Standard Clean-2 (RCA SC-2)

- The mixture includes Deionized Water, H<sub>2</sub>O<sub>2</sub>, and Hydrochloric Acid (Recommended ratios range from 6:1:1 to 60:1:1).
- The following metals and compounds are dissolved by this mixture: Copper, Aluminum, Al(OH)<sub>3</sub>, Fe(OH)<sub>3</sub>, Mg(OH)<sub>2</sub>, and Zn(OH)<sub>2</sub>.
- The substrate will be rinsed in Deionized Water. The substrate will be subjected to an ultrasonic bath for five minutes in order to minimize residue.

#### E. Isopropyl Alcohol (IPA) and Acetone

- Subject the substrate to an ultrasonic bath with IPA for five minutes.
- Subject the substrate to an ultrasonic bath with acetone for five minutes to remove dried water marks.

#### F. Plasma Cleaning

- The PDC-32G models works with the following gases: Ar, H<sub>2</sub>, He, and N<sub>2</sub>. F<sub>2</sub> would not be a viable gas since this gas will be corrosive for the preferred deposition metals.

- Etch rate is about 10 nanometers per minute [8]

#### **D. TERMINATION OF BONDS**

The dangling bonds from the outermost layer of the solid surface arise when the substrate's crystal lattice is disrupted. The surface is more prone to ambient chemical reactions. Various treatments are performed to stabilize the substrate's surface [9].

Silicon surfaces are terminated with  $-H$ ,  $-F$ , and  $-OH$  groups. Hydrofluoric solutions are used to terminate bonds and eliminate oxides. For Silicon (100) substrates,  $SiH_2$  is formed as the Hydrofluoric Acid solution interacts with the Silicon surface's dangling bonds. As etching occurs between the Silicon surface and the Hydrofluoric solution [9], hydrogen termination slows down in the presence of air and water. The Silicon substrate's Silicon-Silicon bonds are prone to interruption by oxygen, while the Silicon-Hydrogen bonds remain stable [10].

Fluorine bonds are formed as the Hydrofluoric Acid solution is introduced to the Silicon substrate. The Hydrofluoric Acid solution causes bond terminations on the Silicon substrate; the concentration of the Hydrofluoric Acid solution determines whether a Hydrogen or Fluorine (dangling) bond will be terminated [10 till 13]. Fluorine bonds are not usually terminated with Hydrofluoric Acid solutions with a potency of 12%; higher potency Hydrofluoric Acid solutions lead to higher chances of terminating Fluorine bonds [14]. Substrate-bound Fluorine bonds are prone to oxidation; Air causes silicon-hydroxyl bonds to form when air interacts with Silicon-Fluorine bonds [10 till 11].

## **E. METAL DEPOSITION OVERVIEW**

Desired patterns are established with Kapton tape; changes are made in the sensor's conductivity or active region. The Gold/ Aluminum/ Gold layer is deposited onto the Silicon substrate [15]. Metal-semiconductor adhesion is ensured as the silicon sensor chips are annealed in either Argon or Helium gas.

### **❖ IN-HOUSE SILICON SENSOR CHIP PROTOCOL**

- Semiconductor Piece [2]
  - Single-strip (2.6 x 1.2 cm<sup>2</sup>) Silicon chips are used for in-house fabrication.
  - Silicon strips are used to bypass the use of prefabricated chips that contain comb-tooth patterns.
  - Each Silicon strip is mounted onto a ceramic-based semiconductor package.
  - The Silicon strips are characterized with the following methods:
    - a.) Raman Spectroscopy
    - b.) Infrared Spectroscopy
    - c.) Scanning Electron Microscopy
    - d.) Dispersive Spectroscopy
    - e.) Current-Voltage Measurements
- Silicon Cleaning Method
  - Silicon strips, both high and low resistivity variants, are cleaned using the AMD (Acetone, Methanol, and De-Ionized Water) method. This method is effective in removing oil and organic molecules.

- Summary of AMD method:
  - a.) Simmer the samples in acetone. The silicon (still immersed in acetone) is subjected to an ultrasonic bath for five minutes.
  - b.) Simmer the samples in methanol. The silicon (still immersed in methanol) is subjected to an ultrasonic bath for five minutes.
  - c.) Simmer the samples in Deionized Water. The silicon (still immersed in Deionized Water) is subjected to an ultrasonic bath for five minutes.
  - d.) After cleaning, further characterization tests were performed. Raman spectroscopy, infrared spectroscopy, and electron dispersive spectroscopy results determined that the clean substrates were Silicon.
- Electrical Characterization
  - Inside the probe station, two probe needles are pressed onto the silicon surface. Resistivity is measured as the probe station is integrated with the Agilent E5272A ammeter.
  - Current-Voltage responses (four-point probe measurements) are derived from the Jandel Engineering four-point cylindrical probe. The Jandel four-point probe device contains its own test device. The test device is home to a current source and a digital voltmeter. With the help of the equipment's software, Dr. Tipton was able to determine the following data: current/ voltage readings, sheet resistance, the wafer's bulk resistivity, and the sensor chip's bulk resistivity.

**F. ANNIE YUNING HSU TIPTON'S Q-DLTS (QUANTUM FINGERPRINT™) PROCEDURE**

- Testing chambers: aluminum enclosure (most common method) and stainless steel bell jars.
- Target species: CO<sub>2</sub>, N<sub>2</sub>, Ar, isopropanol, and ethanol. Different target species are placed in the enclosure, and measurements are performed at the user's preferred times.
- Procedure
  - a.) Substrate regeneration is performed by heating the substrate to 40°C for 5 to 10 minutes. The sample will then be cooled to room temperature.
  - b.) Initial measurements will be performed in an open air environment. The open air measurement serves as the baseline.
  - c.) 1 mL of 1-propanol is introduced into the (Aluminum) enclosure. The measurement for 1-propanol will be collected after 15 minutes.
  - d.) Before other target species are introduced to the enclosure, the substrate will be regenerated by increasing the system's temperature to (35 to 45°C) for 5 to 10 minutes.
  - e.) Another baseline (open air) measurement will be performed.
  - f.) Other target species will be introduced: isopropanol, methanol, butanol, ethanol, and water.

### III. PREPARATION OF BARRIERS

#### A. OVERVIEW

Sufficient rectification is a necessity when dealing with tools that utilize Schottky barriers. Proper rectification is achieved when a high barrier height is established. Figure one shows that most metals can produce Schottky contacts [1].

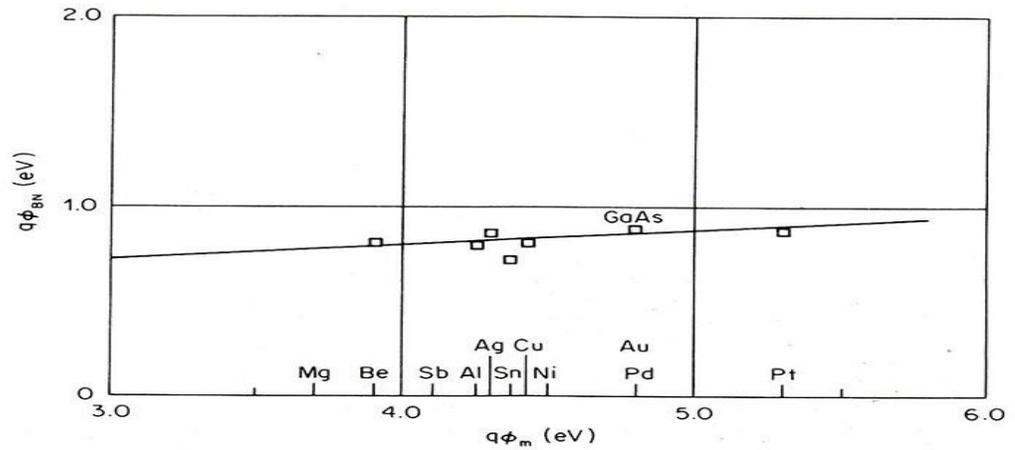


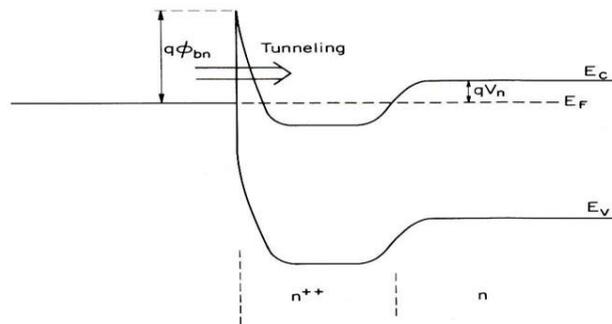
Figure 1. Graph of metal/ Gallium Arsenide barrier height for various depositions.

Preparing Schottky barriers, in a vacuum environment, leaves a lot of room for uncertainty. Uncertainty lies in the film's appearance, the metal-semiconductor interface, and impurities. When depositing a metal layer on Gallium Arsenide (Table 1), a thin oxide layer will form on the surface. Interface uncertainties would lead to different Schottky barrier heights across the wafer. Oxide layers alter the electrical properties and the metallurgical behavior of the metal- semiconductor interface. The deposition of metals upon a semiconductor, at the vacuum range of  $10^{-6}$  to  $10^{-7}$  torr, introduces oxygen onto the metal film. Oxygen will alter the silicide reaction rates and the phase growth sequence [1].

Table 1. Notable Metallizations with Gallium Arsenide (Schottky Contacts) [1]

Metallization	Temperature (°C)	Barrier Height (eV)	Analysis	Degradation Details
Aluminum	200	0.8	Secondary Ion Mass Spectroscopy and X-Ray Diffraction.	Slight Gallium and Arsenic Outdiffusion.
Nickel/ Gold	RT to 350		Rutherford Backscattering Spectrometry, Equivalent Porous Media	No Nickel accumulation at Gold/ Gallium Arsenide interface.
Platinum/ Nickel	RT to 200	0.88	X-Ray Diffraction	No Reaction
Platinum/ Nickel	380-480	0.95		GaPt, PtAs <sub>2</sub> , and Ga <sub>2</sub> Pt are formed
Titanium-Tungsten/ Titanium	Temperature when contact is formed	0.8	Scanning Electron Microscope-Energy Dispersive Spectroscopy	High leakage current due to damage induced by sputter deposition. Lower leakage currents are seen for evaporated depositions.
Tungsten/ Silicon/ Tungsten	Temperature when contact is formed		Auger Electron Spectroscopy, Scanning Electron Microscope	Weak channeling pattern: polycrystalline Tungsten is found near the surface. Amorphous region is formed at the Tungsten/ Silicon surface.
Tungsten/ Silicon/ Tungsten	500 (about four hours of exposure)		Electron channeling	Metallization becomes amorphous
Aluminum/ Titanium/ Gallium Arsenide	400	0.75	X-Ray Diffraction, Auger Electron Spectroscopy	Al <sub>3</sub> Ti and GaAlAs is formed at the interface.
Titanium-Tungsten/ Silicon/	500 (exposure of four hours)		Auger Electron Spectroscopy,	Metallization becomes amorphous

Ohmic contacts are non-rectifying metal-to-semiconductor contacts. These contacts serve as low-resistance junctions. Ohmic contacts provide conduction, in both directions, between the metal and the semiconductor [17]. It is not feasible to deposit Ohmic contacts onto Gallium Arsenide wafers without forming a dipole layer. Gallium Arsenide wafers have to be doped to a high level before deposition. After deposition, a narrow depletion region and a thin electron barrier will appear. Conduction occurs on thin barriers through tunneling. Figure 2 depicts the tunneling effect [1].



**Figure 6.3 Energy band diagram for a tunnelling metal-/semiconductor contact**

Figure 2. ( $q\Phi_{bn}$  represents the charge of the barrier height.)

The electron barrier becomes thinner as the  $n^{++}$  region is doped (Tables 2-4). Desired Ohmic behavior is achieved when the  $n^{++}$  region is doped to the level of  $5 \times (10^{19})$  donors/  $\text{cm}^3$  [1].

Table 2. Ohmic Contacts and their Corresponding Barrier Heights at 300 Kelvin [17]

Metal	Barrier Height (eV)
Aluminum	0.8
Gold	0.86
Nickel	0.83
Platinum	0.86
Gold/ Gallium	0.71 to 0.75
Gold/ Germanium	0.27 to 0.35
Gold/ Tin	0.72
Platinum/ Nickel	0.95

Table 3. Gallium Arsenide Ohmic Contact Depositions (P-Type) [17]

Metal System	Composition
Silver/ Indium	25% Indium, alloy 500°C
Silver/ Indium/ Zinc	80% Silver, 10% Indium, 10% Zinc, alloy 600°C
Silver/ Zinc	90% Silver, 10% Zinc, alloy at 450°C
Gold/ Beryllium	1% Beryllium

Table 4. Gallium Arsenide Ohmic Contact Depositions (N-Type) Williams [17]

Deposition	Comments
Silver/ Indium	75% Silver, 25% Indium; Sinter (made from powder) 500°C
Silver/ Indium/ Germanium	90% Silver, 5% Indium, 5% Germanium; Alloy 600°C
Gold/ Germanium/ Nickel	12% Germanium (alloy), Ni; Alloy 480°C
Gold/ Silicon	Alloy 425°C
Gold/ Tin/ Nickel/ Gold	Alloy 300°C
Indium	300°C melt
Indium/ Aluminum	Alloy 320°C
Indium/ Gold	90% Indium; Alloy 550°C
Indium/ Nickel	Nickel Plated to Indium
Palladium/ Germanium	Sinter 500°C for two hours
Tin/ Nickel	Nickel plated to Tin; alloyed

## B. SAMPLE PREPARATION

The Gallium Arsenide wafers are cut with a Diamond Saw. The wafers are cut into (1 cm by 1 cm) squares. The Piranha method is used to clean the Gallium Arsenide wafers [18]. The wafers are cleaned with two chemical cleaning solutions and multiple Deionized Water rinses. The solutions are the Dilute Piranha Solution (Sulfuric

Acid, Hydrogen Peroxide, and Deionized Water) and Dilute Hydrochloric Acid Solution. Reagent- grade chemicals will be used in the Piranha cleaning method.

The first chemical cleaning mixture (Dilute Piranha Solution) is comprised of the following proportions: 1 part of Sulfuric Acid, 8 parts of Hydrogen Peroxide, and 500 parts of Deionized Water. The Gallium Arsenide wafers are placed inside the cleaning container. The chemicals will be added in the following order: Deionized Water, Hydrogen Peroxide, and Sulfuric Acid. The wafers can only soak in the solution for 30 seconds.

The wafers are transferred, with the use of tweezers, from the Dilute Piranha Solution to the Deionized Water container. The wafers and tweezers should be soaked in Deionized Water for five minutes. Before being cleaned in the Dilute Hydrochloric Acid solution, the wafers will be rinsed again in a fresh container of Deionized Water for five minutes.

The Dilute Hydrochloric Acid solution is composed of one part Hydrochloric Acid and one part Deionized Water. The wafers and the tweezers will be soaked for two minutes. After the acid clean, the wafers will be rinsed in Deionized Water for five minutes. After the initial rinse, the wafers will be rinsed again in Deionized Water for five minutes. The samples are left to dry.

The depositions are done thru thermal evaporation. Nickel, Germanium, and Gold were deposited onto one side of the Gallium Arsenide wafer. One side of the wafer is blocked off with Kapton tape. About 60% of the evaporator's power were used in each deposition. Table 5 describes the sequence of depositions.

Table 5: Order of Depositions (Substrate: Undoped Gallium Arsenide)

Metal	Thickness (kiloAngstrom)	Max Rate ( $\text{\AA}$ per second)	Power
Nickel	0.056 (uncertainty of 0.002)	1.9	60.00%
Germanium	0.482	1.2	60.00%
Gold	0.547	4.2	60.00%
Nickel	1.50	3.8	60.00%
Gold	0.373	30	60.00%
Nickel	0.494	13	60.00%

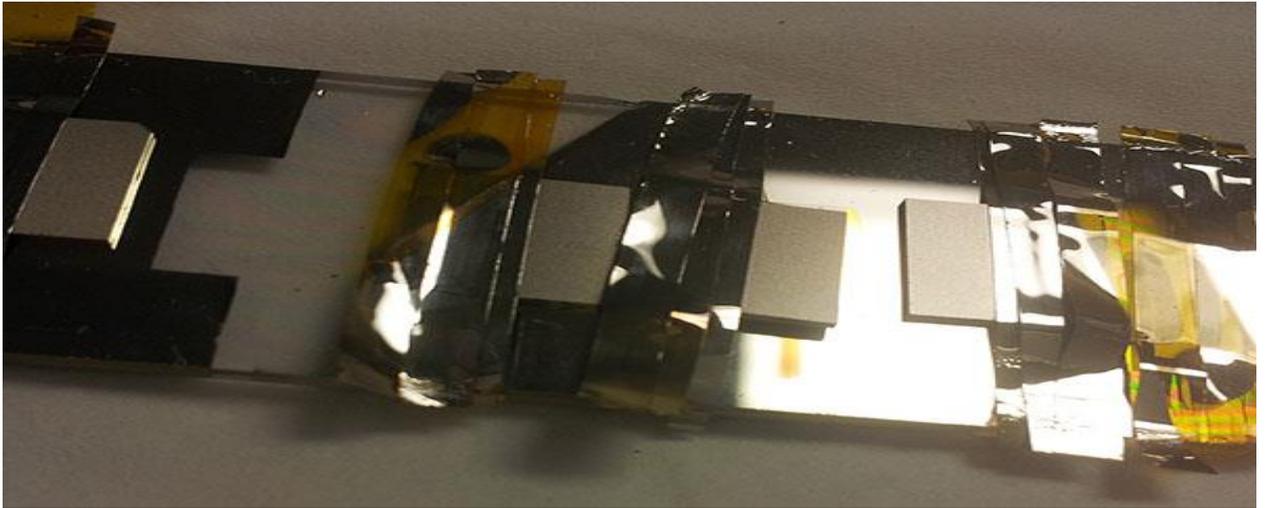


Figure 3. Gallium Arsenide Wafer with Ni/ Ge/ Au/ Ni/ Au/ Ni contact

Before any analysis is done, the wafer must be cleaned. Gloves must be worn during the cleaning process. Alconox detergent is used to clean off the Kapton tape residue. Inside a beaker, the detergent is dissolved in deionized water. The residues are cleaned off by rubbing the solutions onto the solution by hand. After the wafer is rinsed with Deionized Water, Reagent- Grade ethanol is imparted on the wafer. Reagent- Grade ethanol removes unwanted residue and evaporates easily. Figure 3 shows a GaAs wafer with contacts.

#### IV. RESULTS

Testing is done using an analysis chamber and Quantum Fingerprint™ hardware. Each side of the wafer is subjected to the analysis chamber's Tungsten needles (Ohmic contact and undoped Gallium Arsenide). The following IV curve (Figure 4 and 5) displayed sufficient characteristics that the metal contact depicts the presence of a barrier above 5 volts. During analysis, the contact between the undoped Gallium Arsenide and the Tungsten needle serves as the Schottky contact.

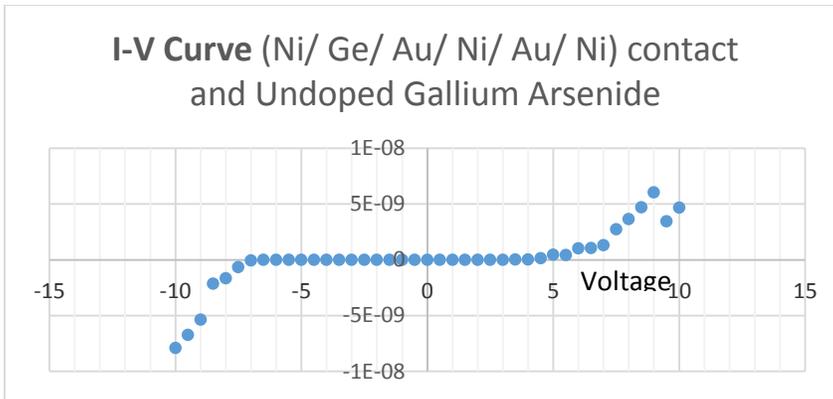


Figure 4.1 IV curve for the GaAs wafer.

The charge separation of 10 volts indicates the possibility that a Quantum Fingerprint™ Signal can be found (Figure 5).

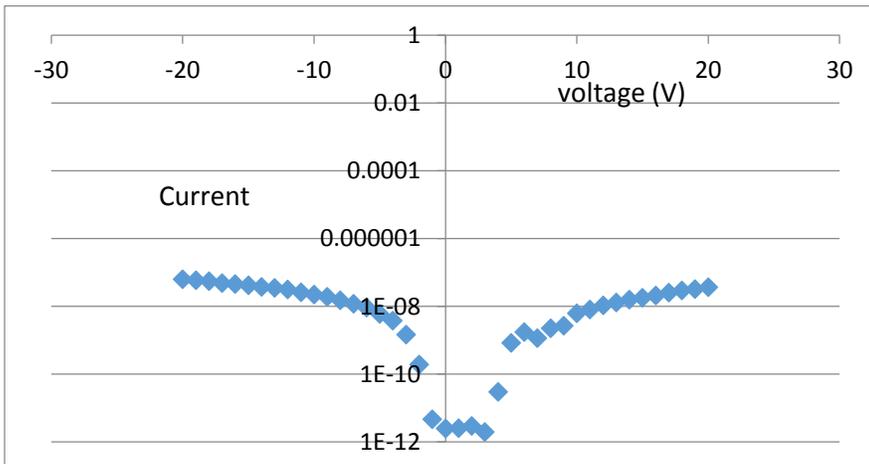


Figure 4.2 IV curve for the GaAs wafer.

Charge Based Transient Level Spectroscopy is used to find the energy levels displayed by materials that are deposited onto the substrate (Figure 6). The measurement is performed in room temperature and the sensor chip is exposed to air. These energy levels act as charge traps. The charge traps produce transient signals when the energy levels calm down after its excited state. A signal was found with the following parameters: charging time of 20000 microseconds, delay time of 500 microseconds, period of 200 milliseconds, 10 microseconds, and 100 averages.

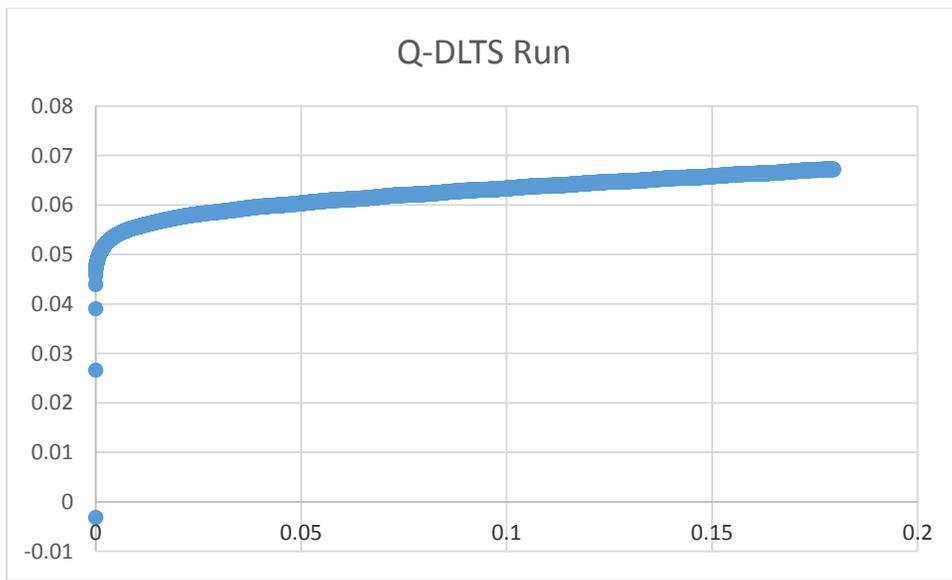
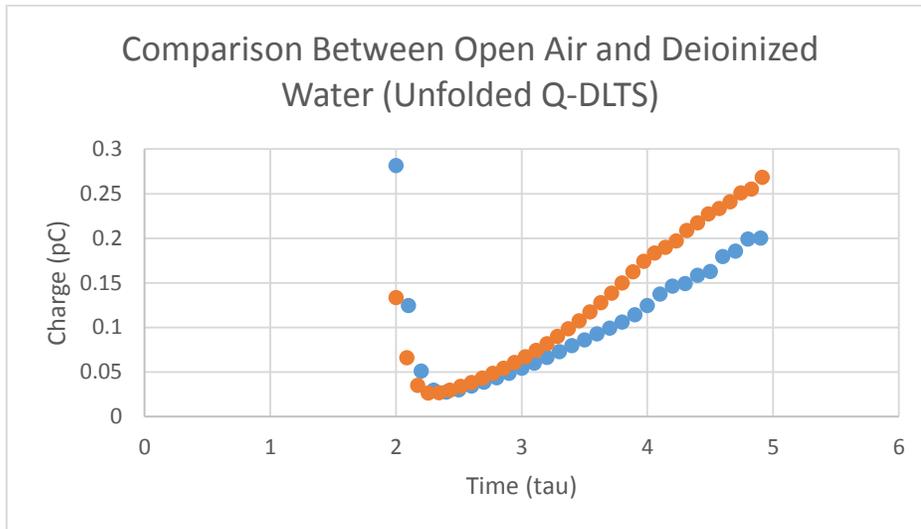


Figure 4.3 QDLTS of the GaAs wafer (Open Air- Base Line). The exponential rise is due to electron leakage from the surface traps formed by molecules absorbed on the GaAs surface.

The following graphs show processed data after the Fourier Transform.

Figure 7 shows the relationship between time ( $\tau$ ) and charge. Blue dots resemble the measurements of open air surroundings while the orange dots resemble the measurements for deionized water.

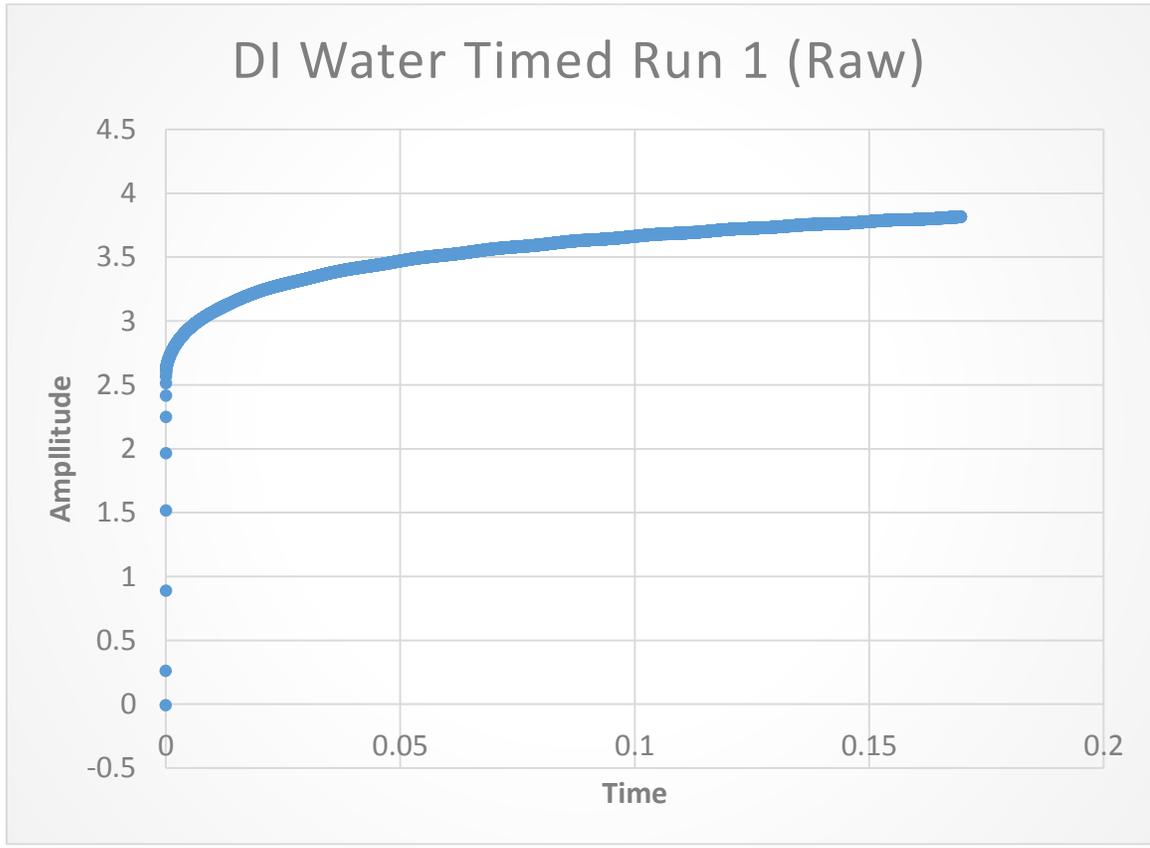


The following runs depict the unfolded data for elapsed-time runs.

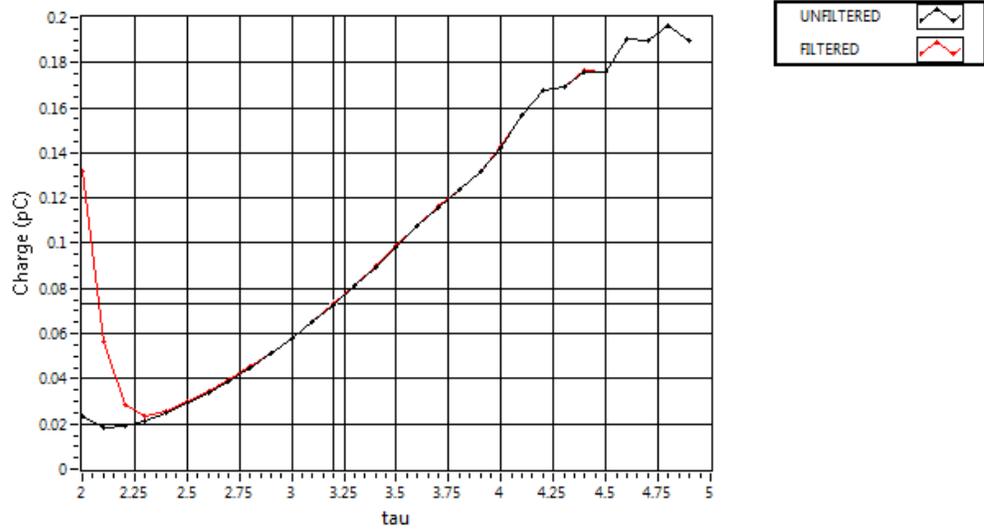
Deionized water is treated as the target species. Raw data was gathered with the following parameters: charging time of 30000 microseconds, delay time of 400 microseconds, period of 200 microseconds, resolution of 10 microseconds, and 1000 averages. Each measurement took 6 minutes and 43.7 seconds. Data was manually recorded every eight minutes. Each data series corresponds to a time interval: 0 minutes, 8 minutes, 16 minutes, 24 minutes, 32 minutes, and 40 minutes.

The unfolded Quantum Fingerprint™ Data was processed in the following circuit parameters: feedback capacitance 100 pF and an amplifier gain of 20. A first order Butterworth filter was used together with a cut off frequency of 10000 Hertz. The following Quantum Fingerprint™ parameters were observed: rate window start time of 100 microseconds (tau- initial), rate window stop time of 100000 microseconds (tau-final), and 30 spectral points in the x-axis.

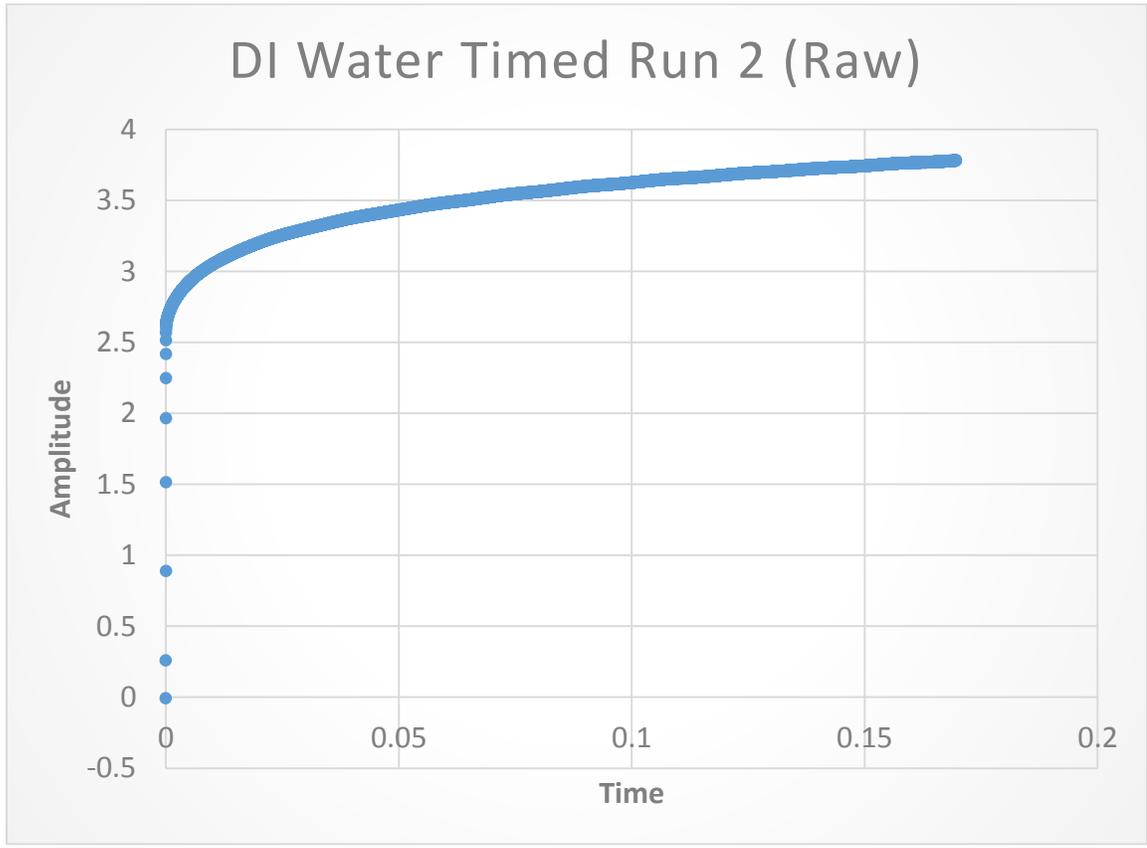
TIMED RUN 1 (ELAPSED TIME: 0 MINUTES)



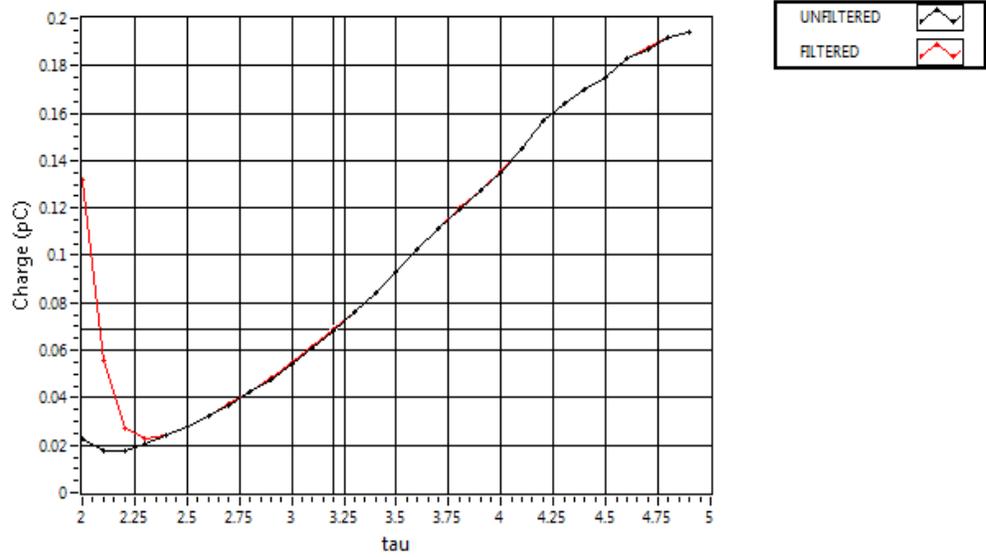
QDLTS of



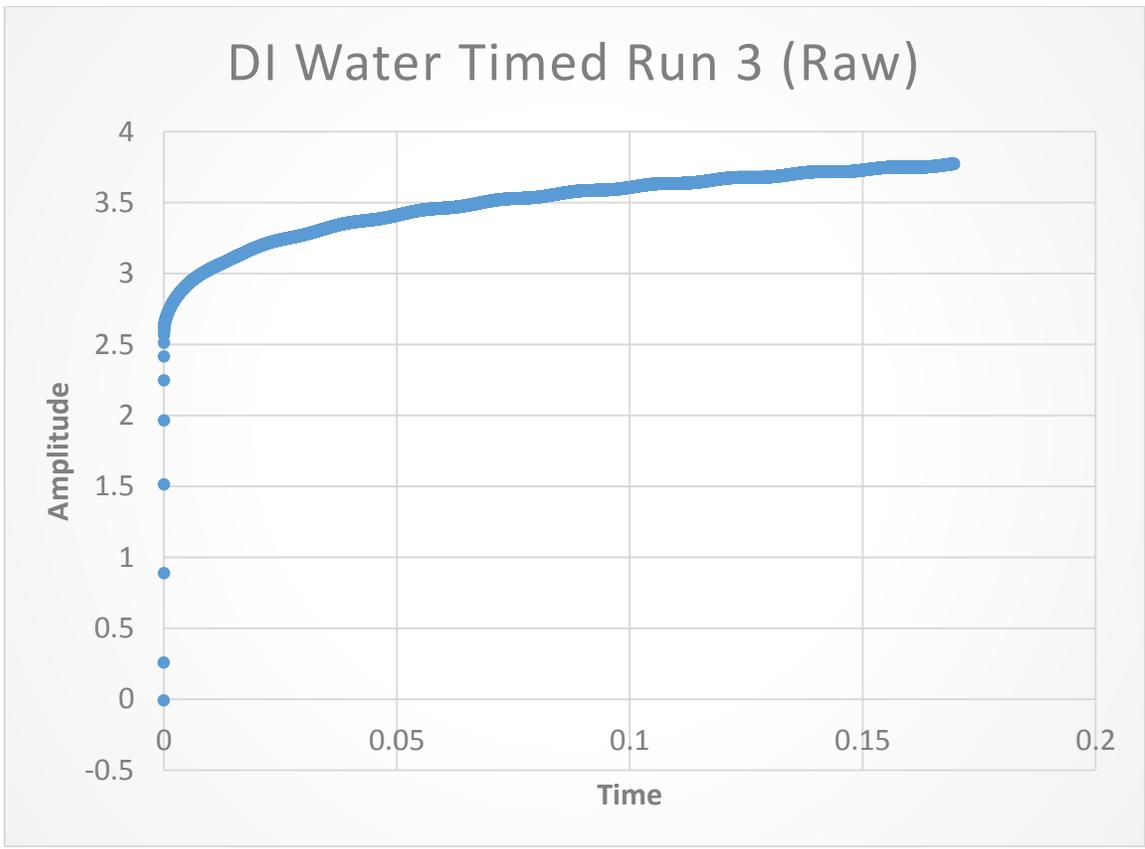
TIMED RUN 2 (ELAPSED TIME: 8 MINUTES)



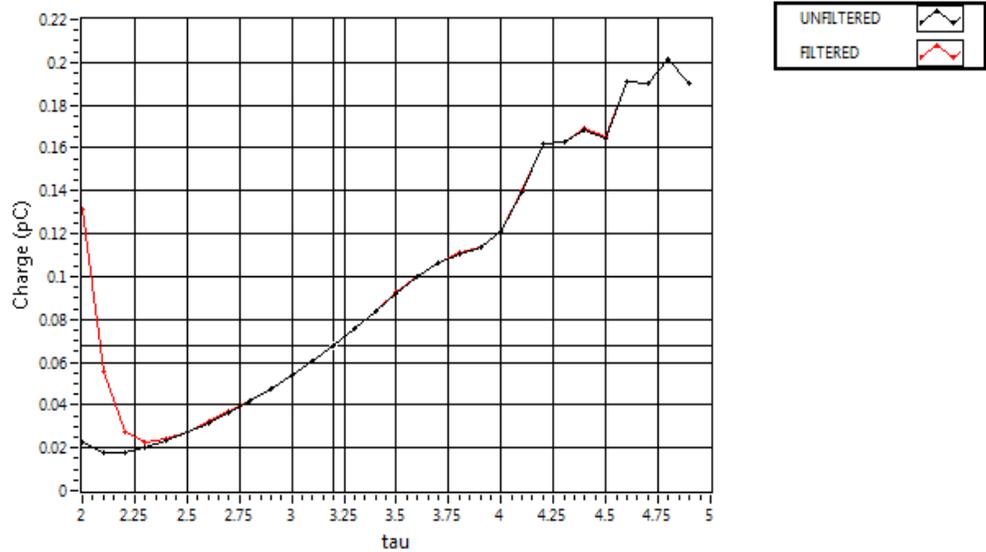
QDLTS of



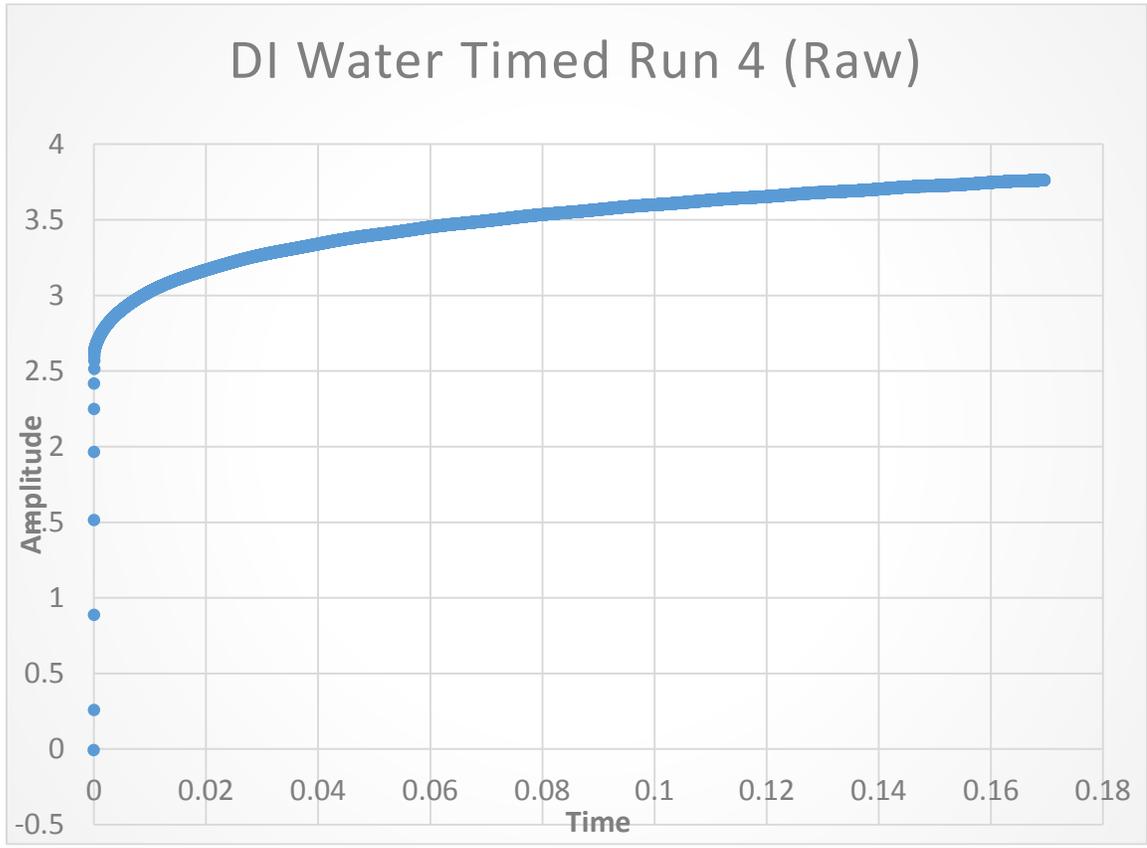
TIMED RUN 3 (ELAPSED TIME: 16 MINUTES)



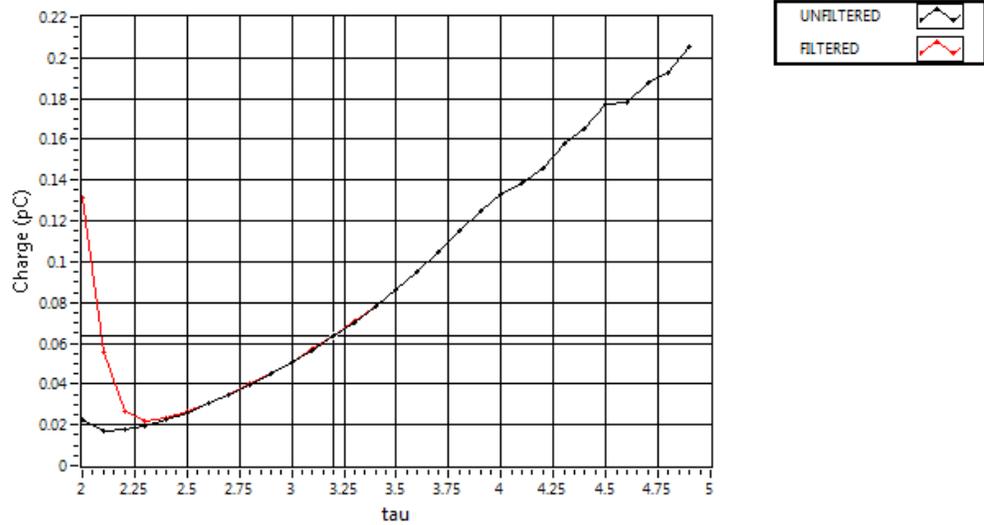
QDLTS of



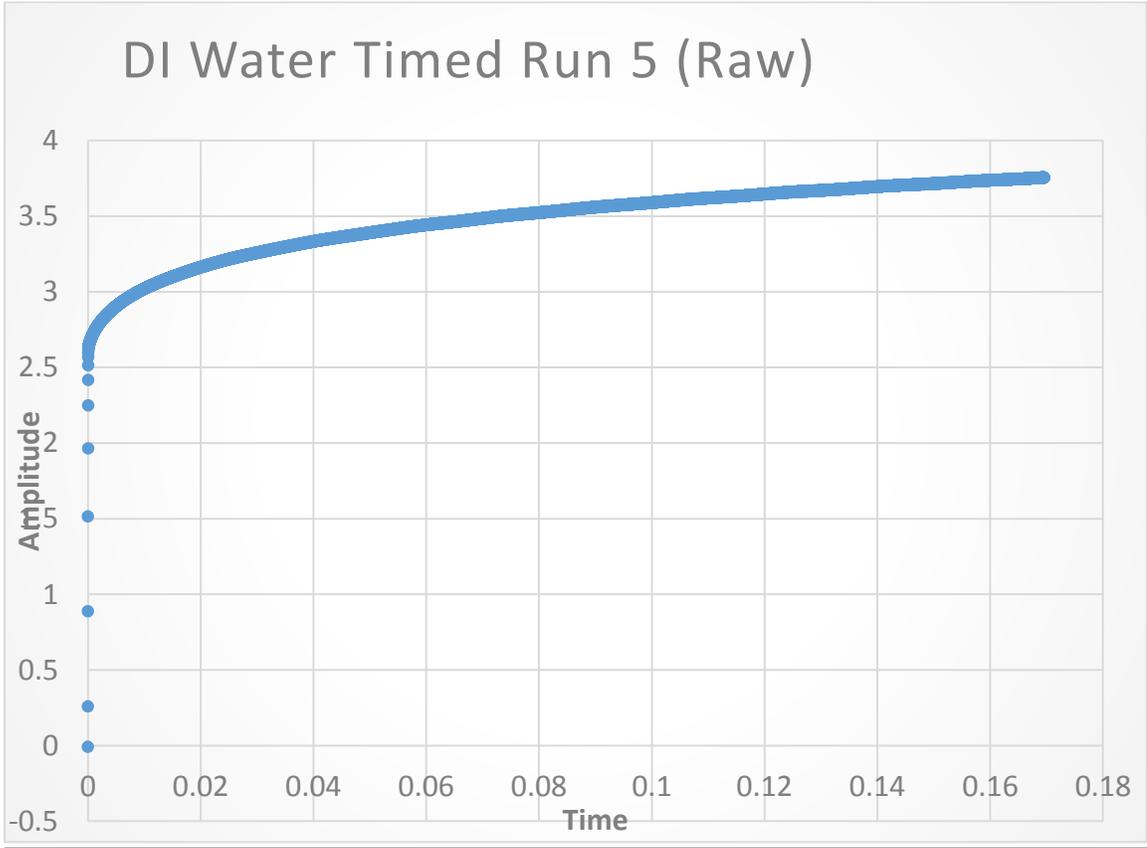
TIMED RUN 4 (ELAPSED TIME: 24 MINUTES)



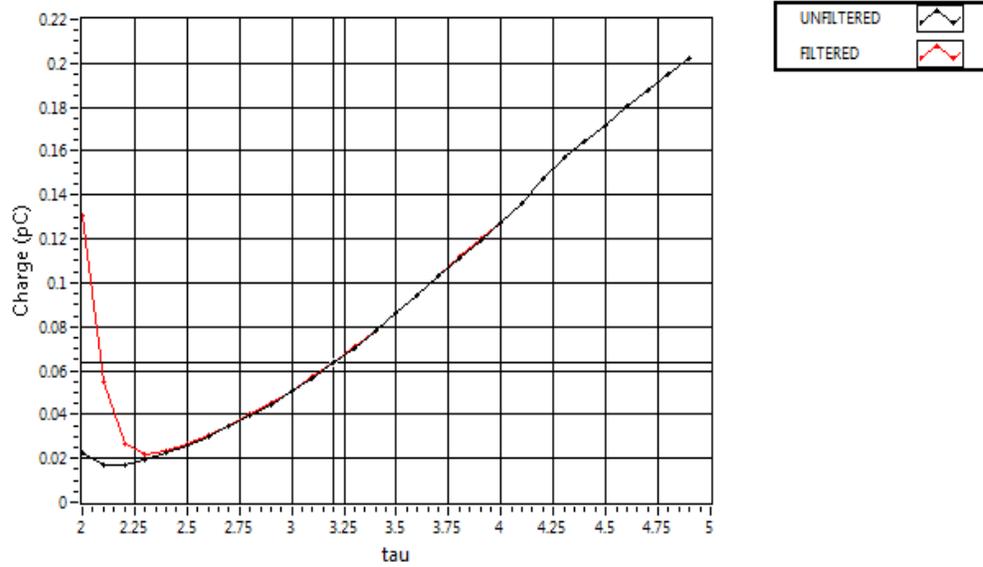
QDLTS of



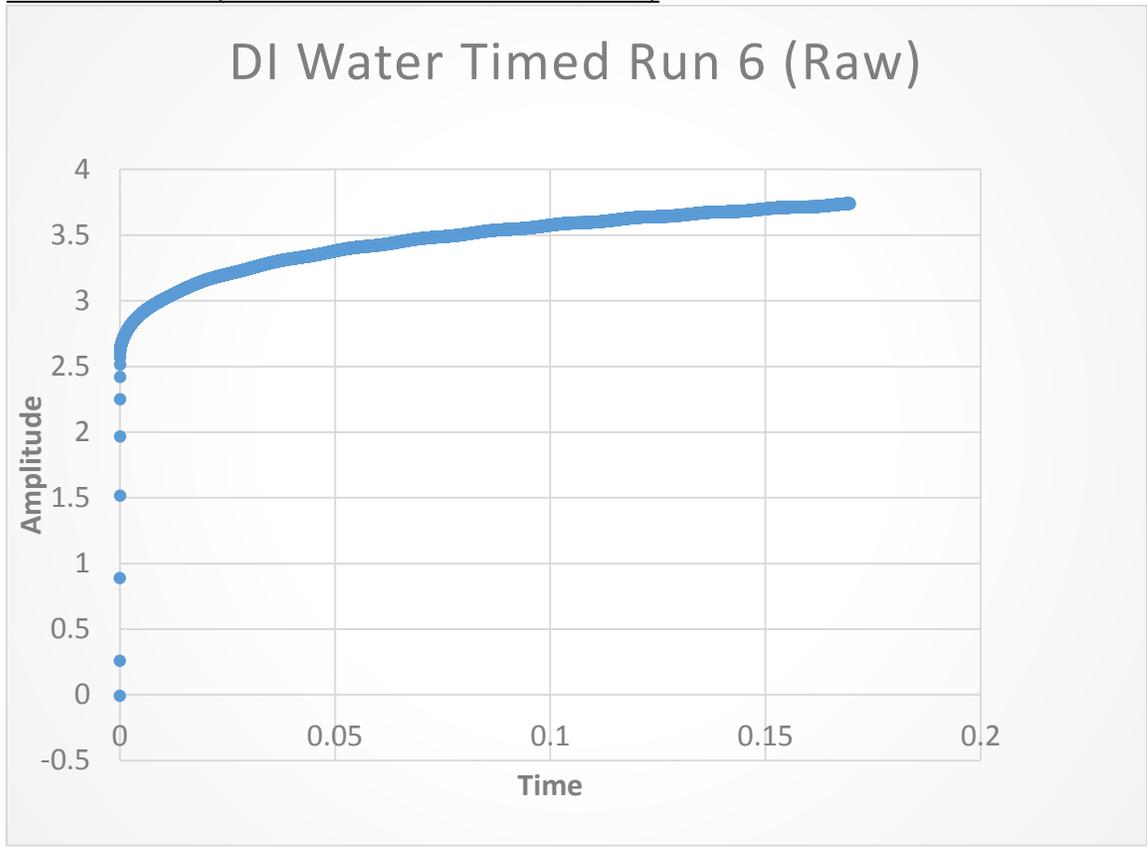
TIMED RUN 5 (ELAPSED TIME: 32 MINUTES)



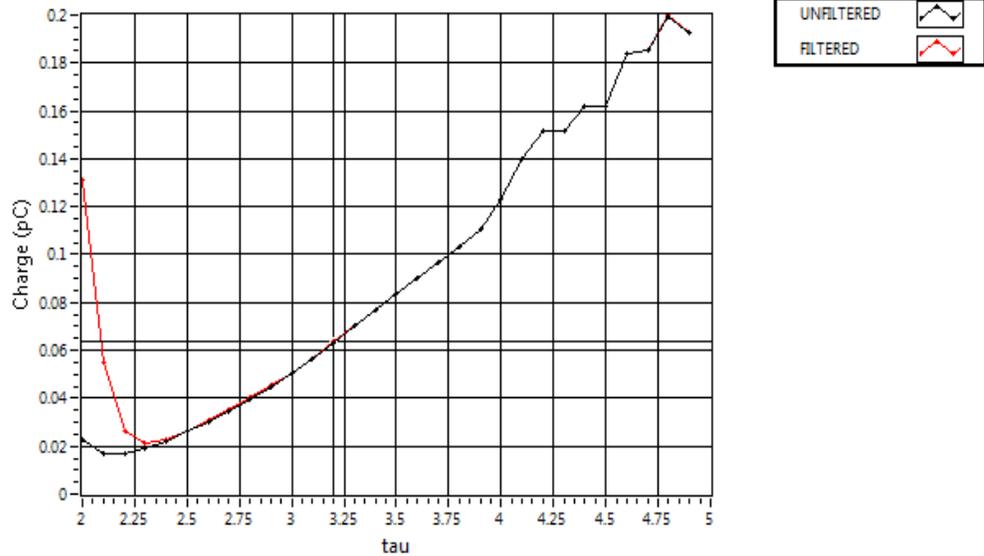
QDLTS of



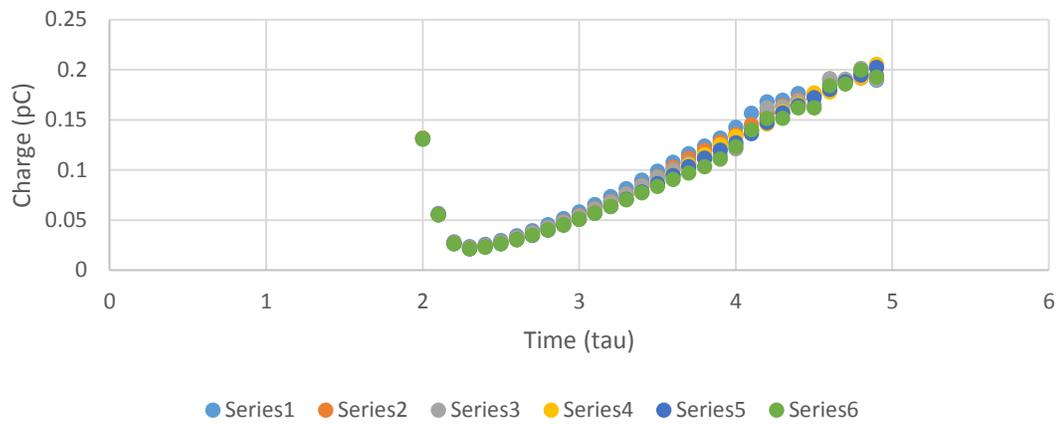
TIMED RUN 6 (ELAPSED TIME: 40 MINUTES)



QDLTS of



### Unfolded Deionized Water Quantum Fingerprint Data (Composite)



## V. CONCLUSION

After several methods of cleaning and metallizations, a method was achieved to produce interfaces that is used for the Quantum Fingerprint™ chemical detection system. Cleaning is an integral part of wafer preparation. Any organic or ionic layer leads to unsuccessful contact preparations. Cleaning methods that involved Piranha solutions (with higher acid concentrations) and acetone proved to be too abrasive for Gallium Arsenide. The Piranha method is effective in removing grease and contaminants [18]. A prominent example is provided by the formation of Ohmic contacts (substrate: Undoped Gallium Arsenide, contact: Nickel/ Germanium/ Gold/ Nickel). An R-squared value of 0.993 is received from the Linear Regression of the Ohmic contact's I-V curve.

Conventional Quantum Fingerprint™ substrates require Ohmic and Schottky contacts. The proposed sample requires less preparation time than conventional Quantum Fingerprint™ substrates, since only one contact is deposited. The interaction between the Tungsten needle and the undoped Gallium Arsenide served as the Schottky barrier. A viable signal was received when the sensor chip was analyzed.

Unfolded Quantum Fingerprint™ data was obtained from raw data gathered at eight-minute time intervals. Deionized water is used as the target species. Noticeable differences in charge measurements (pC) were found over time. Concerns are seen as the raw data measurements are susceptible to electrical noise. Physical shock also impairs raw data acquisition.

Improvements in chamber design and metal-semiconductor interface integrity must be made in order for Gallium Arsenide to become a contender for an optimal chemical detector interface. Better chamber designs allow the user to introduce target species into the analysis chamber efficiently. Modified analysis chambers also allow the

user to gather Quantum Fingerprint™ spectra at different pressures and temperatures. The conscious effort to monitor the sensor chip's integrity is vital since the substrate's lattice and dangling bonds allow for unwanted reactions to occur.

## REFERENCES

- [1] Howes, M. J.. "Metallizations for GaAs Devices and Circuits." *Gallium arsenide: materials devices and circuits*. Chichester: Wiley, 1985. 195-254. Print.
- [2] An Exploration of Chemical Agents Detection Using the Quantum Fingerprint™ Technology. Tipton, Annie Yuning Hsu, 1979- (University of Missouri- Columbia, 2009).
- [3] S. Wartewig. *IR and Raman Spectroscopy*. Wiley-Vch, 2003.
- [4] J. Goldstein, D. Newbury, D. Joy, C. Lyman, P. Echlin, E. Lifshin, L. Sawyer, and J. Michael. *Scanning Electron Microscopy and X-Ray Microanalysis*. Springer, 3rd edition, 2003.
- [5] [www.jandel.co.uk](http://www.jandel.co.uk), Accessed Date: May 10th, 2009.
- [6] P. Van Zant. *Microchip Fabrication*. McGraw-Hill, 2004.
- [7] W. Kern. Overview and evolution of semiconductor wafer contamination and cleaning technology. In W. Kern, editor, *Handbook of Semiconductor Wafer Cleaning Technology – Science, Technology, and Application*, pages 3-67. Noyes Publications, 1st edition, 1993.
- [8] Harrick Plasma, 120 Brindley St. Ithaca, NY 14850. *User's Manual for the Basic Plasma Cleaner PDC-32G (115V) or PDC-32G-2 (230 V) (and Optimal Plasmaflo)*.
- [9] X. G. Zhang. *Electrochemistry of Silicon and its Oxide*. Kluwer Academic/ Plenum Publishers, 2001.
- [10] M. Ikeda, S. Iwamoto, and N. Nagashima. Behavior of fluorine on silicon (100) surfaces etched with NH<sub>4</sub>F aqueous solutions. *Electronics and Communications in Japan*, 83:41-48, 2000.
- [11] T. Takahagi, A. Ishitani, and H. Kuroda. Fluorine-containing species on the hydrofluoric acid etched silicon single-crystal surface. *J. Appl. Phys.*, 69:803-807, 1991.
- [12] K. Ljungburg, U. Jansson, S. Bengtsson, and A. Soderberg. Modification of silicon surface with H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>:HF and HNO<sub>3</sub>:HF for water bonding applications. *J. Electrochem. Soc.*, 143:1079, 1996.
- [13] M. Werner. Ohmic contacts. In J. G. Webster, editor, *Wiley Encyclopedia of Electrical and Electronics Engineering*, volume 15. Wiley, 1999.
- [14] T. Takahagi, I. Nagai, A. Ishitani, and H. Kuroda. The formation of hydrogen passivated silicon single crystal surfaces using ultraviolet cleaning and HF etching. *J. Appl. Phys.*, 64:3516, 1988.
- [15] Y. C. Yu. Electron tunneling and contact resistance of metal-silicon contact barriers. *Solid-State Electron*, 13:239-247, 1970.
- [16] *Semiconductor Physics and Devices*. New York: McGraw-Hill, 2003. Print.
- [17] Williams, Ralph E.. "Ohmic Contacts." *Gallium Arsenide Processing Techniques*. Dedham: Artech House, 1984. 232-233. Print.
- [18] White, Robert. "GaAs Wafer Prep (Piranha followed by Hydrochloric)." Tufts University. [http://engineering.tufts.edu/microfab/index\\_files/SOP/GaAs\\_wafer\\_prep\\_SO.P.pdf](http://engineering.tufts.edu/microfab/index_files/SOP/GaAs_wafer_prep_SO.P.pdf)