Development and Testing of Low-Cost Hydrogen Leak Detection

Cooperative Research and Development Final Report

CRADA Number: CRD-16-613

NREL Technical Contact: William Buttner

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Cooperative Research and Development Final Report

Report Date: June 26, 2018

In accordance with requirements set forth in the terms of the CRADA agreement, this document is the final CRADA report, including a list of subject inventions, to be forwarded to the DOE Office of Science and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

Parties to the Agreement: Element One, Inc.

CRADA Number: CRD-16-613

CRADA Title: Development and Testing of Low-Cost Hydrogen Leak Detection

Joint Work Statement Funding Table showing DOE commitment:

Estimated Costs	NREL Shared Resources a/k/a Government In-Kind
Year 1	$125,000.00
TOTALS	$125,000.00

Abstract of CRADA Work:

Element One, Inc (Element One), and the National Renewable Energy Laboratory (NREL) cooperated to facilitate the development of novel hydrogen detection technology by providing Element One. access to unique NREL resources and core capabilities in hydrogen technology and material characterization.

Summary of Research Results:

Element One has developed a unique sensor platform for the selective detection of hydrogen. The sensor is based on chemo-chromic materials that react in the presence of hydrogen at ambient temperature to change both its color and electrical conductivity. As a colorimetric indicator, the presence of hydrogen can be detected visually without any supplemental electronic detection instrumentation. Alternatively, conductivity changes can be measured with simple electronic detection technology (e.g., resistance) for a low-cost electronic sensing element with the potential for remote interrogation via integration with radio frequency identification (RFID) technology. The sensor consists of a substrate, hydrogen-sensitive material (active material), and a protective coating. The active material and coating can be configured as either a thin- or thick-film, which have distinct fabrication procedures. Thick films are typically formed via manual fabrication methods (e.g., screen printing, "painting"), while thin-films are fabricated using sophisticated vacuum deposition technologies. Thin-film fabrication has precisely controlled physical features (e.g., film thickness, geometric features, and to some extent, micro-crystalline morphology), requires less material (which is often expensive), and device fabrication can be scaled up for large-scale production to better exploit economy of scale manufacturing for lowering unit cost. Although specialized equipment is needed for thin-film depositions, such technology is standard, and more importantly, available in the NREL Sensor Laboratory (see Figure 1). One advantage of Element One's low-cost leak detection technology is that the sensors can be economically deployed. The sensor can be interrogated by visible inspection, and or potentially configured for remote integration using RFID technology. To expand its market and applications, Element One explored new materials and fabrication parameters for improved sensor performance and for compatibility in harsh environments (elevated temperatures, liquids and corrosive environments).

The NREL Sensor Laboratory was awarded a Small Business Voucher (SBV) Award with Element One. Formalization of this partnership was through CRADA-16-613 between the NREL Sensor Laboratory and Element One. The purpose of this CRADA effort was to facilitate the development of novel hydrogen detection technology by providing Element One access to unique NREL resources and core capabilities in hydrogen detection technology and material characterization. In this collaboration, the NREL sensor laboratory provided access of its resources to Element One to advance the development of its hydrogen sensor technology. NREL support provided to Element One under this CRADA included:

- Access to and maintenance of specialized equipment owned by NREL that required by Element One to fabricate hydrogen-sensitive thin-films
- Provided access to NREL facilities for physical characterizations of the Element One thin films sensing elements (e.g., scanning electron microscopes, imaging optical microscopes)
- Supported new market development for the Element Hydrogen Technology (e.g., explore unique applications, such as transformer oil integrity). Interactions including cross-DOE/NREL program discussions, such as with Art Anderson of the National Wind Technology Center
- Use of the sensor laboratory resources (space, equipment, gas cylinders, and personnel) for evaluation of the thin-film sensing element.

Figure 1: The NREL Varian Model 3118 Thermal Evaporator (housed in the NREL Sensor Laboratory) is a physical vapor deposition system for thin-film fabrication.

Specific activity and outcomes performed by NREL and Element One under the auspices of CRADA 16-613 are provided below.

Task 1: Fabrication and Physical Characterization
The NREL Sensor Laboratory provided critical resources to allow Element One to fabricate and characterize its thin-film hydrogen sensing element prototypes. Initial support provided by NREL was to adapt available capabilities to better accommodate the production requirements for the Element One sensing element. At the start of the contract, several hardware issues were identified with the Varian Model 3118 Thermal Evaporator, which although minor, would affect reliable production of thin-films. This included the maintenance on the gate valve to the deposition chamber and some electrical upgrades to assure more controlled depositions. Work to implement these upgrades was subcontracted to Rodney Smith, who with gany years of experience on the Varian Model 3118, could efficiently and economically perform this task. As part of this upgrade process, Dr.Smith provided documentation on the and internal design (wiring schematic) and standard operation of the Varian thermal evaporator (see Appendix A).

NREL provided the resources to maintain the operation and reliability of the Varian Thermal Evaporator throughout the CRADA partnership, including a thorough cleaning the vacuum bell jar. This allowed for improved assurances of thin film purity, and hence potentially improved sensor reliability by eliminating chemical impurities which might be present it the system from previous project. Cleaning was performed by glass beads and required removal of the bell jar from main system. Upon completion, reassembly was required to remount the bell jar, which was followed by reassembly and system check for vacuum leaks and other function checks.

NREL also provided resources to Element One to characterize the physical morphology of the films by SEM or optical microscopes. Figure 2 shows SEM images. Too thick of films resulted in a proclivity to crack while too thin of films tended to have poor electrical continuity. Film thickness had to be controlled for optimal performance.

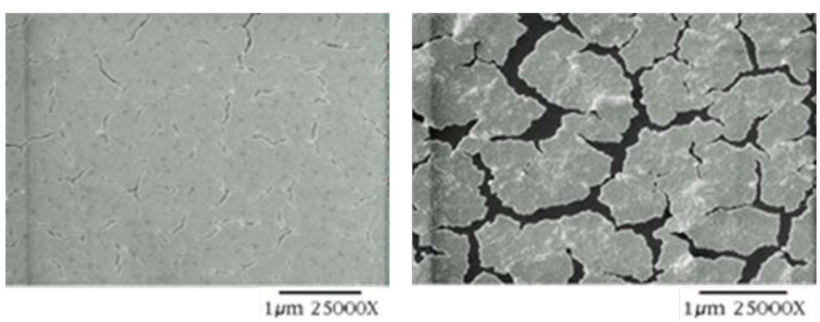

Figure 2: SEM images of Element One hydrogen-sensitive thin films performed at NERL under CRADA 16-613

Further details on Sensor Fabrication and Physical Characterizations were provide by Element One in their final report.

Task 2: Basic Assessment of Sensor Performance
The Element One thin film sensor can be probed via either a colorimetric transduction (readily detected by visual inspection) or an electronically. The electronic detection is noted for increased sensitivity and for the potential for remote interrogation. The electronic transduction process requires simply a means to measure a change in thin film resistance. This is conveniently achieved

providing the sensors are fabricated on to a substrate that provides electrodes (e.g., interdigitated electrodes), such as that shown in Figure 3). These can be obtained from commercial suppliers. Substrates from various suppliers were used.

Figure 3: Commercially-available substrate with interdigitated electrodes for thin-film resistance measurements

These substrates readily accommodate prototype sensing elements via thin-film fabrication protocols. However, the resulting layered structure requires a special fixture for accommodating the gas exposure requirements with the electronic signal. NREL assisted in the design of a test cell holder for Element One sensors (see Figure 4), which was fabricated by the NREL machine shop. This cell was a flow-through design, in which the test gas was continuously flowing directly over the sensing element. The test gas composition could be changed quickly (e.g., from an air background to a hydrogen-containing test gas). This cell design was used extensively by Element One to characterize the response of its sensing element.

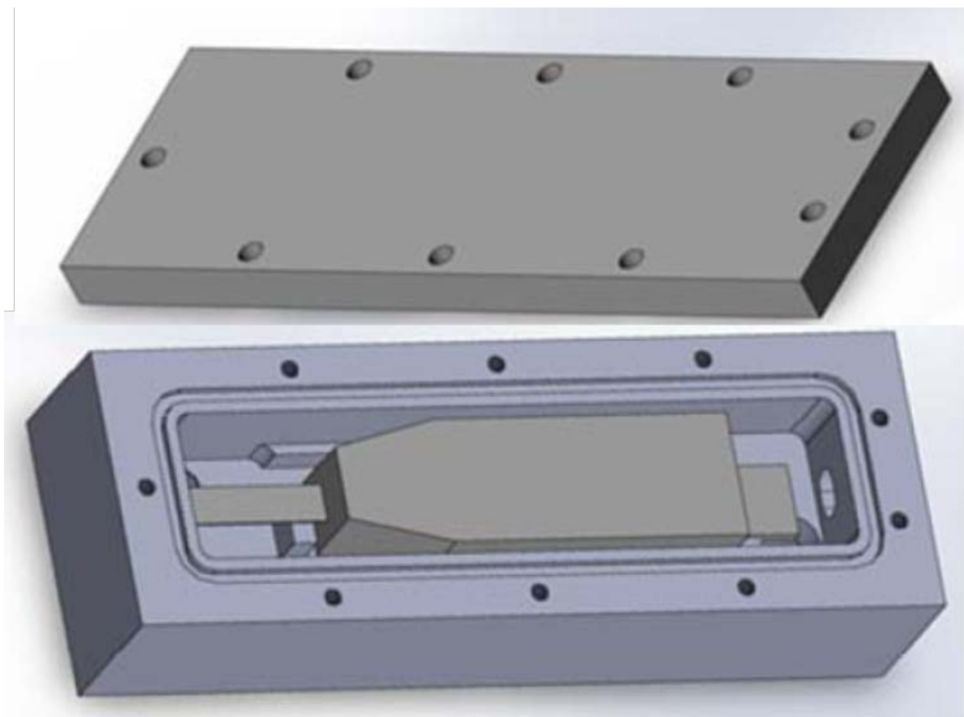

Figure 4: Design of a test cell holder for Element One sensors fabricated on to a substrate with indigitated electrodes. The test cell holder was fabricated by the NREL machine shop

The NREL sensor laboratory also provided independent sensor testing of the Element One sensing elements. The NREL sensor laboratory also evaluated the Element One sensing element prototypes using a test apparatus with a gas exposure chamber. This system could precisely control the test conditions, including environmental parameters (temperature, pressure, humidity) chemical composition of the test gas, while logging the sensing response into an electronic data file for record keeping and analysis. One critical parameter that the NREL sensor test apparatus can easily perform is the short-term repeatability of the device to repetitive hydrogen exposures. This test, performed in the NREL Sensor Test Apparatus, is shown in Figure 5. As indicated, this configuration of the Element One sensor does show good reproducibility, which confirms that the sensor is reversible.

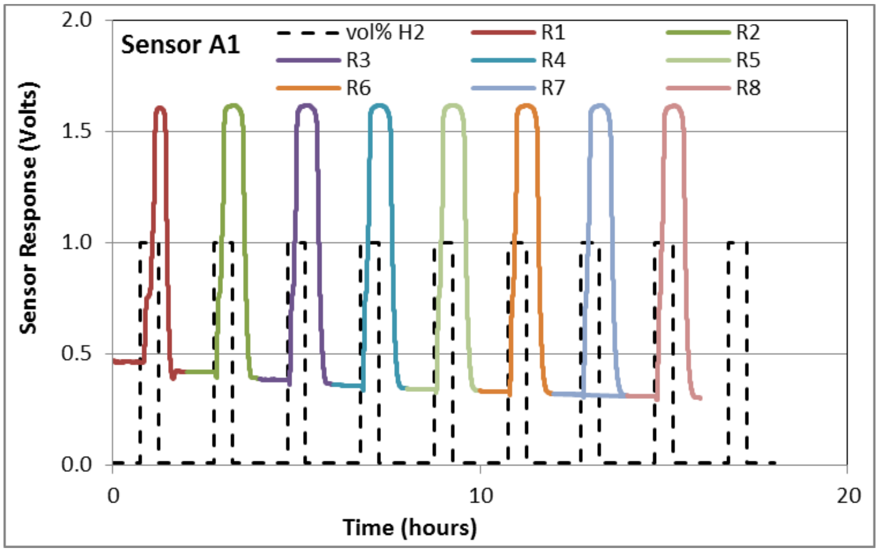

Figure 5: Demonstration of the response repeatability for the reversible Element One Sensor. Testing was performed in the NREL Sensor Test Apparatus

Task 3: Impact of Environmental and Chemical Stresses

Multiple samples of the Element One sensing elements prototypes were tested in the NREL sensor test laboratory under various chemical environments. Specifically, these sensors were exposed to several chemical impurities. Impurities may have no impact, may look like a hydrogen exposure (e.g., an interferent), or may damage the sensor (e.g., a poison). The specific interferents were: 100 ppmv carbon monoxide (CO), 1 vol% methane (CH4), 100 ppmv ammonia (NH3), 10 ppmv nitrogen dioxide (CO2), and 1000 ppmv carbon dioxide (CO). Figure 6 shows the results of the interferent exposure. Several of the impurities (CO, CO2, CH4) had no effect, one impurity (NH3) appeared to be an interfent, and one impurity (NO2) looked like a poison. The impact of an impurity may be minimized by proper selection of a protective coating.

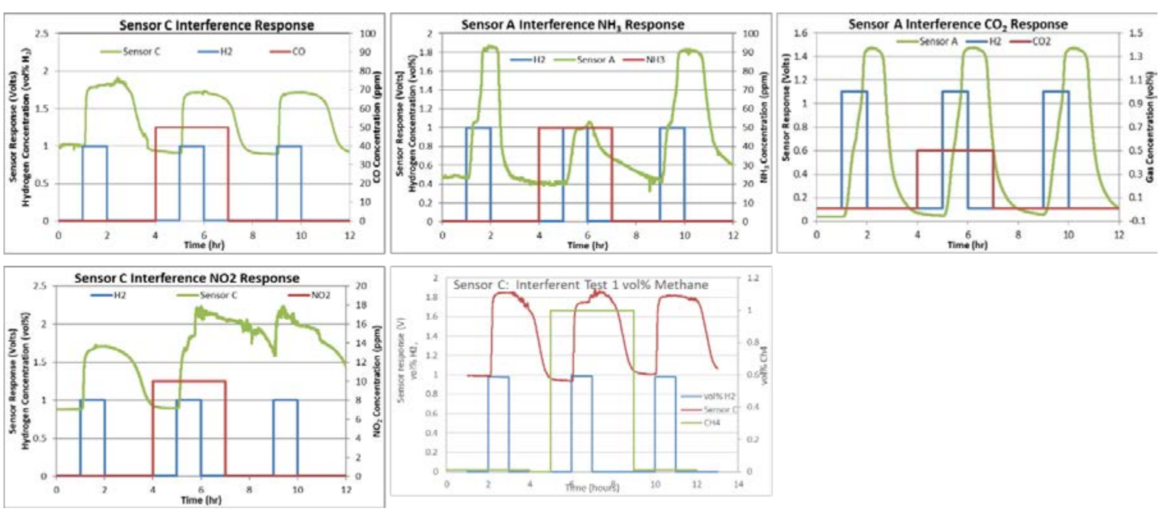

Figure 6: Impact of chemical stressors on the Element One Sensor stability. Some common impurities (CO, methane, CO2) had no effect, while ammonia had a reversible impact, and NO2 was a poison.

Task 4: Sensor Deployments and Application Development
Element One is exploring a configuration of their unique thin film platform to quickly detect hydrogen in transformer oil. The presence of hydrogen is an indication that the oil is breaking down and this may ultimately compromise the insulating properties of the oil, which in turn can result in catastrophic transformer failure. Hydrogen detection is an indication of the integrity of the oil. Presently this is done in the laboratory, but the Element One concept can make for a low-cost field screening tool This application was reviewed within NREL for the power electronics of wind turbines. Although, the concept was viewed interesting, it was not within the scope of the NREL Wind Program. However, Element One is pursuing this market with private companies.

Task 5: Reporting
NREL and Element One worked together during the duration of the SBV collaboration (CRADA 16-613) with regular meetings to review project progress, test results, and to provide partners updates on the sensor testing and development. The updates were held regularly in the form of teleconference calls or written reports. Element One provided a comprehensive final report. This work formed the basis of a follow-up collaborative STTR proposal, which was, regrettably, not funded. However, NREL and Element One are pursuing other opportunities for development of this technology, specifically the RFID configuration and new markets.

Subject Inventions Listing:

None

Responsible Technical Contact at Alliance/NREL:

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Name and Email Address of POC at Company:

William Hoagland, whoagland@elem1.com

DOE Program Office:

DOE Small Business Vouchers Pilot (Sarah Truitt, Pilot Manager)

Appendix A:
Standard and Safe Operation Procedures for the Varian Model 3118
(Sub-contract Deliverable to NREL under the SBV

Varian Model 3118 Thermal Evaporator

Standard/Safe Operating Procedures

Element One, Inc.

Standard Operating Procedure

I. Description

The thermal evaporator is used to deposit solid dielectrics or metals onto substrates. Evaporation is done under high vacuum in a water cooled bell jar chamber. Evaporation is achieved by heating a filament source (evaporation boat). As the source material evaporates, it forms a thin film on the samples. The evaporation rate is varied by adjusting the power with an external rheostat (Variac) controller. The overall system consists of a vacuum pumping station and a physical vapor deposition subsystem.

The vacuum pumping station consists of a large liquid nitrogen-cooled diffusion-pumped high vacuum station with a separate mechanical roughing pump. The cabinet in which the diffusion vacuum pump is housed includes the electro-mechanical valves and electronic vacuum gauges which control the operation of the vacuum system. An external tank of liquid nitrogen is necessary for to provide cooling to the baffle of the diffusion pump during vacuum depositions. An external tank of compressed nitrogen gas is used to refill the vacuum deposition chamber after a thin film device is deposited.

The working chamber in which the vapor depositions occur consists of a large water-cooled stainless-steel bell jar (approx 18-inch diameter by 24 inches high) which sits on top of the vacuum pumping system cabinet. The bell jar has a motorized lift. Inside the bell jar are supports for sample holders; high current, low voltage electrical feed troughs; and a holder for a quartz crystal deposition rate monitor.

A Variac variable output voltage transformer connected to a voltage step-down transformer, both exterior to the vacuum system cabinet, are used to manually adjust the low-voltage, high current electrical power to the evaporation sources inside the bell jar. The quartz crystal deposition rate monitor electronics are also mounted external to the vacuum system cabinet.

Materials are vaporized in sequence from three separate electrically heated sources near the base of the working chamber and the vapors from these sources are condensed onto substrates near the top of the chamber. The large distance from vapor source to the substrate holders is necessary to produce a relatively uniform deposition thickness over the area of the substrate. The quartz crystal monitor inside the working chamber is used to monitor the deposition rates and to estimate the final thicknesses of the thin films that are deposited. Experimental thin film gas sensors are typically deposited as multiple-layer devices by sequentially evaporating materials such as tungsten oxide, palladium metal and poly tetra-fluoro-ethylene polymer—each layer being deposited at a different source temperature, at a different vacuum pressure, and at a different deposition rate—in sequence without opening the vacuum chamber.

II. General Safety Precautions

a. If you are evaporating and a building alarm sounds, TURN OFF THE POWER SUPPLY and leave immediately.

b. To prevent sodium contamination, wear poly gloves whenever handling the source metals or the inside of the chamber.

c. Wear Polaroid glasses when viewing the boat to prevent eye damage.

d. Do not operate equipment without back and side panels in place.

III. General Restrictions/Requirements

a. Must be a qualified user

b. Fill out the logbook (sample log) for each use.

IV. Required Utilities/Services

a. Compressed air: ~50 psi to operating pneumatic valves.

b. Cooling water: Approximately 0.2 gpm @ 70 degrees F.

c. Exhaust gases from vacuum pump to building exhaust ventilation (non- hazardous)

d. Liquid nitrogen (LN_2) Dewar.

e. Electrical Connections:

- Vacuum Pump 230 or 460 Volts, 3 phase, ~ 10 amp.
- Thermal Evaporator: 208-240 Volts, single phase, 50 amp.
- Instrumentation: 120 Volts, single phase, <20 amp.

V. Definitions

a. Ion gauge filament—Measures the pressure of the chamber while pumping with the diffusion pump.

b. Base plate—Located inside the chamber and holds the metal sources (boats).

c. Sample holder—Fixture that holds the substrates inside the chamber.

d. Shutter—A metal paddle that will cover/uncover the source metals (not installed on this unit).

VI. Setup/Sample Loading Procedure

a. Open the water valve to the thermal evaporator. Ensure flow meter is set for approximately 0.2 gpm (located on back of the unit).

b. Make sure the fore line switch is set to "OPEN".

c. Switch the "AIR RELEASE" toggle switch to "ON". This will vent the bell jar in approximately 3-5 minutes.

d. Switch the "AIR RELEASE" toggle switch to "OFF" to close the VENT.

e. To raise the bell jar, move the toggle to the LEFT on the HOIST control. Only raise bell jar enough to load the sample. NOTE: If the bell jar is raised too far, the hydraulic hoist will become jammed.

f. Clean the base plate around the edge where it meets the gasket, the gasket and the inside of the bell jar using a lint free cloth and isopropyl alcohol (IPA).

g. Load the sources into the electrodes on the base plate (up to four). Four sources can be loaded, and the source changed using the "SOURCE SELECTOR" knob.

h. Load the substrates onto the holder. The perforations are designed to hold samples 2 inches in length and width.

i. Check the readout on the crystal monitor. If the reading is less than 5.910, the crystal needs to be replaced.

j. Lower the bell jar by moving the toggle to the "RIGHT" on the "HOIST" control. Stop 2-3 inches short, and ensure that the bell jar is aligned evenly, then push toggle the "DOWN" button again until it is completely closed.

VII. Operating Procedure

a. Open the LN_2 line using the solenoid switch. The cold trap takes about 10 minutes to fill; this can be done at the same time that the samples are being loaded.

b. To begin pumping down the bell jar: hold the viewing window firmly against the O-ring, close the fore line and open the rough pump valve. Once pumping begins the window should remain sealed against the O-ring.

c. When the pressure gauge is reading below 100 mTorr on the rough vacuum gauge, close the rough pump valve, open the fore line and then the high vacuum valve (in that order). After pumping for a few minutes (~5 min) with the diffusion pump, turn on the ion gauge filament. A sufficient vacuum can be reached after 3 to 4 hours. The minimum pressure to operate is $6x10^{-5}$ torr.

d. Select the correct program on the crystal monitor for the material to be evaporated. "TOOLING", "DENSITY" and "ZRATIO" are characteristics of the evaporant, and should already be entered into the program.

e. Wait for the bell jar to pump down to the desired pressure.

f. Zero the readout on the crystal monitor.

g. Make sure the source selector is set to the correct position.

h. Water doping: For introducing water into WO_3 films, slowly open the feed-through knob between the bell jar and the leak valve. When the pressure drops down again, slowly open the leak valve until a pressure of 5E-5 torr is achieved.

i. Slowly increase the power to the electrodes by turning the Variac to the right. Once the source starts evaporating, adjust the power level to achieve the appropriate deposition rate. (For WO_3 the rate should be around 5 Å/sec.)

j. After the desired thickness is reached, turn the Variac control to zero. If you are going to evaporate from another source, set the source selector to the appropriate position and load the correct program on the crystal monitor.

VIII. Post Operation Shutdown Procedure

a. If depositing WO3, close the leak valve and the feed-through knob. (The leak valve is completely closed at a setting of "93". Do not turn the valve any further than this or it will be damaged.)

b. Close the high vacuum valve.

c. Turn the ion gauge filament "OFF."

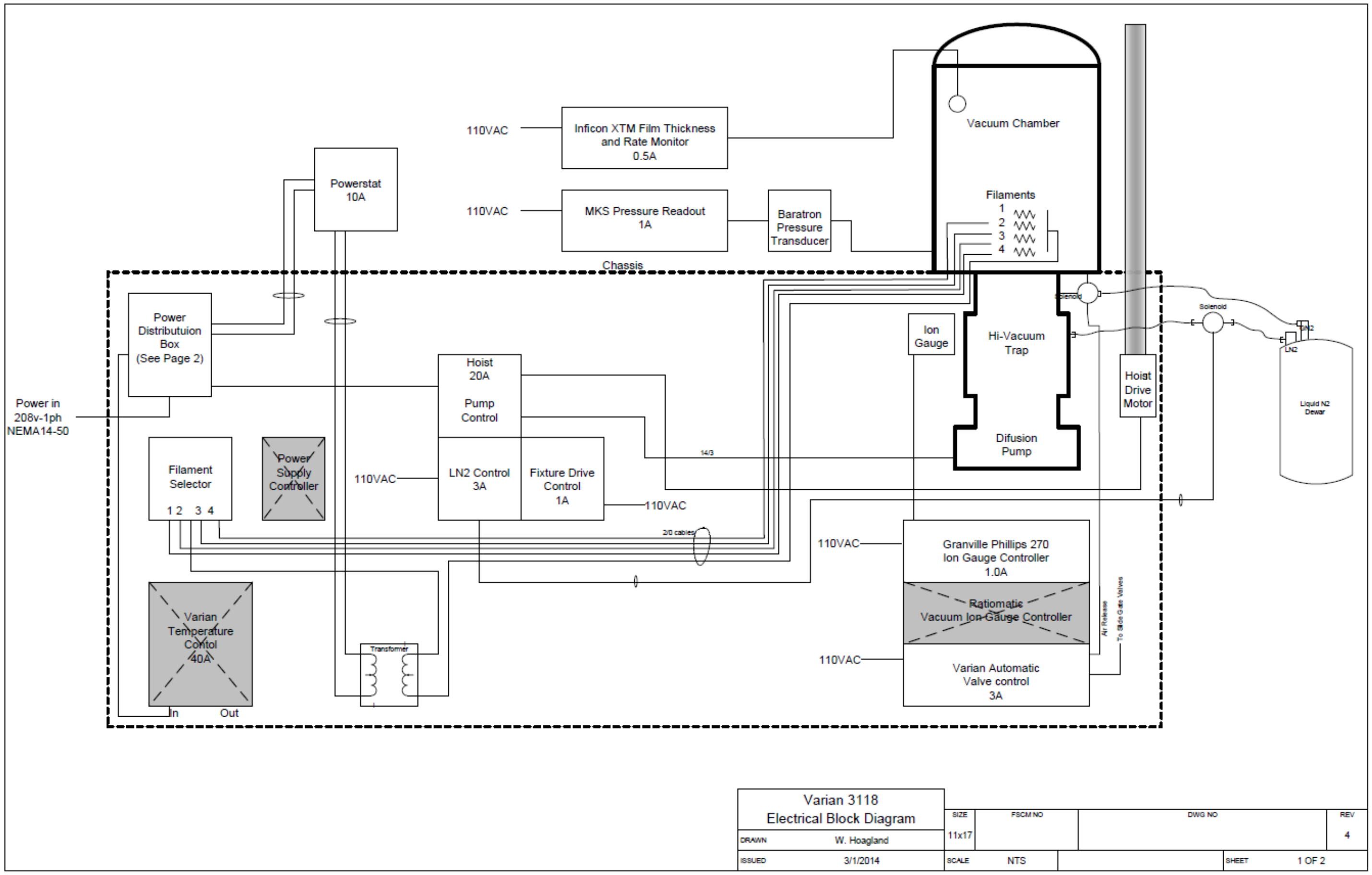
d. IMPORTANT: WAIT 20 MINUTES BEFORE YOU TURN THE COOLING WATER OFF to allow the filament and sources to cool.

e. Switch the "AIR RELEASE" toggle switch to ON using nitrogen to vent the bell jar in after approximately 3-5 minutes.

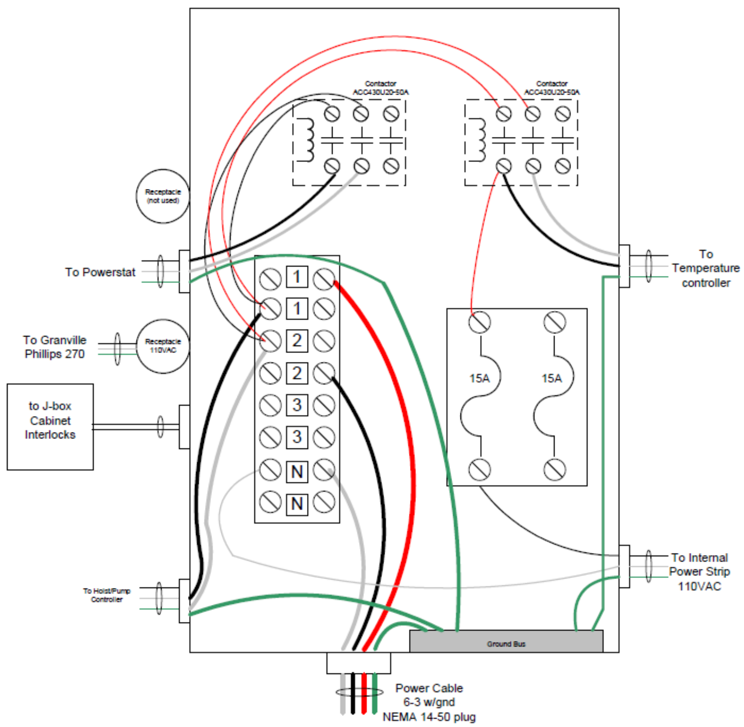
f. Raise the bell jar by pushing the "RAISE" button on the "HOIST" control, and then remove your samples and the source(s). To close, stop 2 -3 inches short, and ensure that the bell jar is aligned evenly. Toggle the "DOWN" switch again until it is completely closed and operate the rough pump to pump the system back down to 100 mTorr as described above.

g. In the event of an emergency, turn off all power to the system and – location specific emergency procedures.


varian
3118
CHAMBER
FORELINE
270 GAUGE CONTROLLER
GRANVILLE-PHILLIPS
Pascal = mbar x 10^2
ON
TC1
TC2
ZERO
POWER
DEGAS
ON/OFF
FILAMENT
ADJUST
EMISSION
PRESSURE IN torr
UP
RANGE
AUTORANGE
NOT IN USE
FORELINE
varian
RANGE
ION GAUGE
TC 1
TC 2
Ratiomatic
843 VACUUM IONIZATION GAUGE
MODE
AUTO SEQUENCE
START
STOP
MANUAL VALVES
varian



110VAC
Inficon XTM Film Thickness and Rate Monitor 0.5A
Vacuum Chamber
Powerstat 10A
110VAC
MKS Pressure Readout 1A
Baratron Pressure Transducer
Filaments
1
2
3
4
Chassis
Power Distributuion Box (See Page 2)
Ion Gauge
Hi-Vacuum Trap
Hoist Drive Motor
Hoist 20A
Pump Control
Power in 208v-1ph NEMA14-50
Difusion Pump
Filament Selector
1 2 3 4
Power Supply Controller
110VAC
LN2 Control 3A
Fixture Drive Control 1A
110VAC
Granville Phillips 270 Ion Gauge Controller 1.0A
Ratiomatic Vacuum Ion Gauge Controller
110VAC
Varian Automatic Valve control 3A
Varian Temperature Contol 40A
In
Out
Varian 3118
Electrical Block Diagram
DRAWN
W. Hoagland
ISSUED
3/1/2014
SIZE
11x17
FSCM NO
DWG NO
REV
4
SCALE
NTS
SHEET
1 OF 2



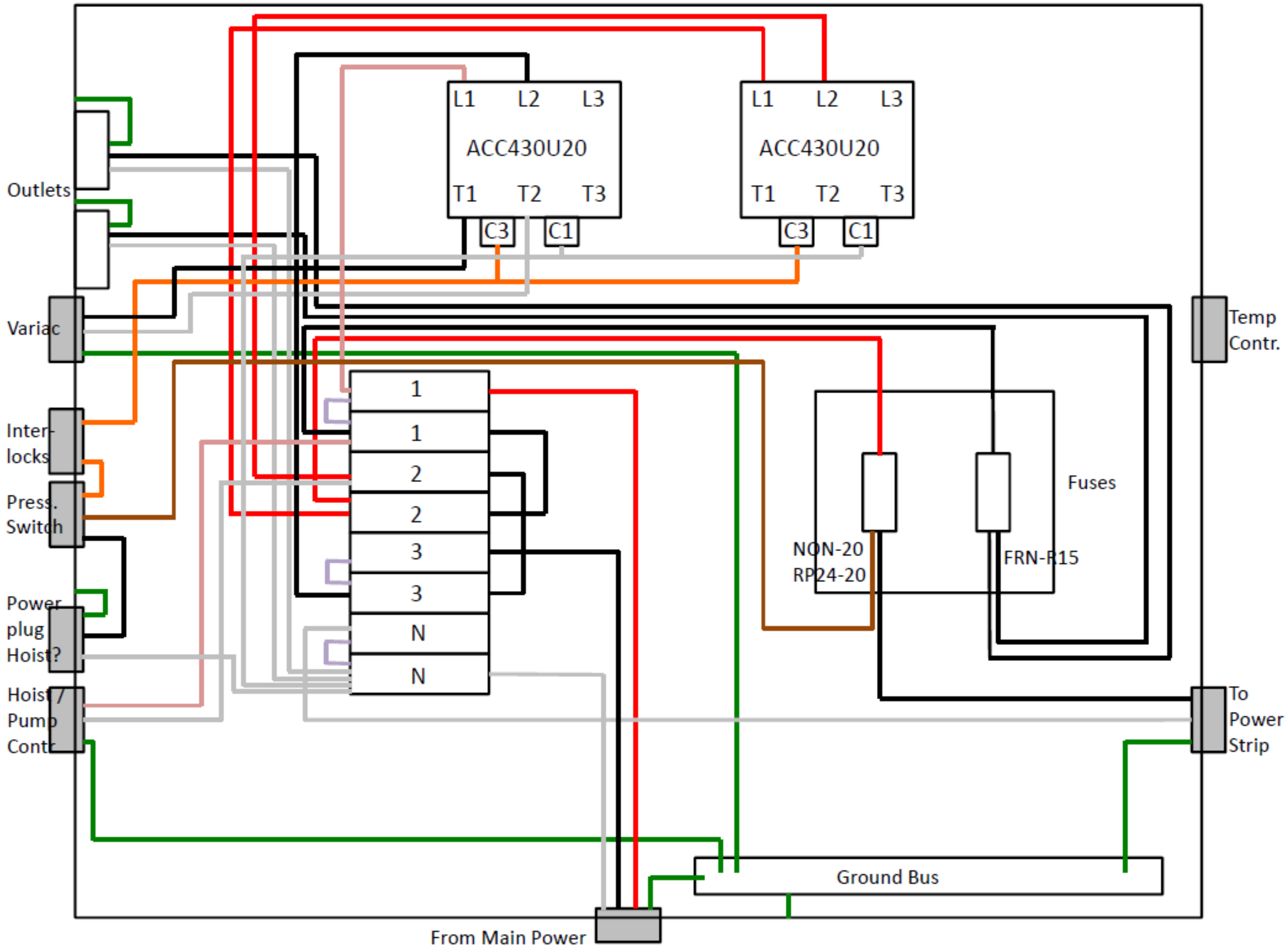
Varian 3118 Power Distribution Schematic (to be verified)

Electrical Components - Current Demand

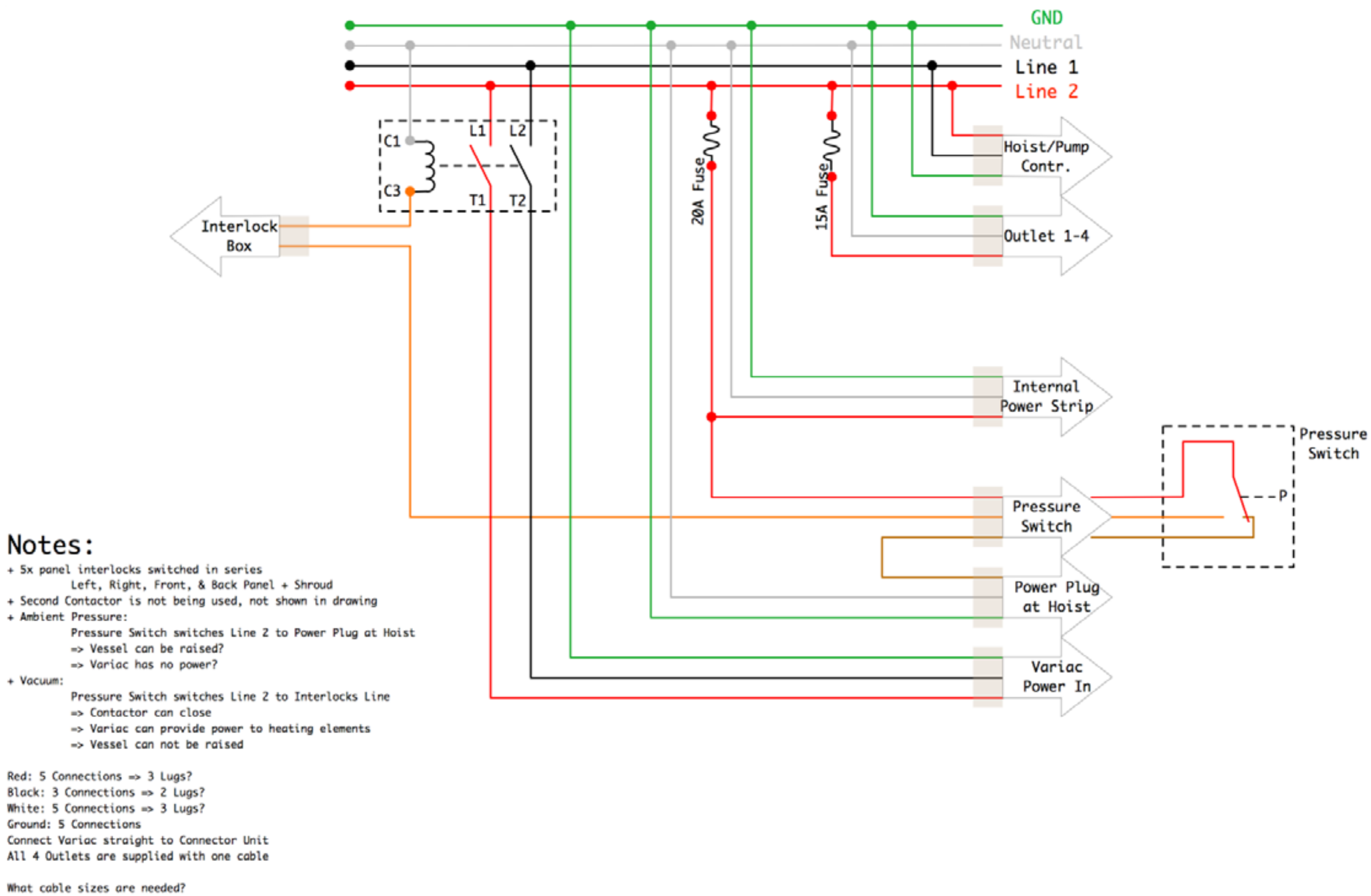
Item Description	Max Amp. Start	Max Amp. Use	Remarks
Varian Power Supply Control	-----	-----	Not in service (replaced by Powerstat)
Difusion Pump/Hoist Control	20A	15A	Hoist amps max. estim. Diff Pump 1875 Watts
LN2 Control	3A	3A	
Fixture Drive Control	-----	-----	Not connected
Automatic Valve Control	3A	-----	Start-up only
Granville Phillips Ion Gauge Controller	1A	1A	Replaces *Rationmatic*
Ratiomatic Vacuum Gauge Controller	-----	-----	Not Connected
PowerStat - 208VAC	-----	10A	External
Inficon XTM Thin Film Thickness and Rate Monitor - 110VAC	0.5A	0.5A	External
MKS Pressure Readout - 1210VAC	1A	1A	External
Varian Temperature Control- 2 08 V	-----	-----	Not Connected
Total Varian	28.5A	30.5A	208-1ph
Mechanical Vacuum Pump	8.5 A	8.5A	230/460-3ph
Total*	37 A	39A	230/460-3ph

***Total Estimated Power Use: Varian - 208V-1ph, 23.5A, Vacuum Pump - 230/460V-3ph, ~8.5/4.5A**

Varian 3118 Electrical Block Diagram	SIZE 11x17	FSCM NO	DWG NO	REV 4
DRAWN W. Hoagland				
ISSUED 2/29/2014	SCALE NTS		SHEET 2 OF 2	



140421 Varian DistrBox Cable Routing



140422 Varian Schematic - remodel - Copy.png