Laboratory for Surface and Nanostructure Modification
located in NSERL*
University of Texas at Dallas

*Natural Science and Engineering Research Laboratory (http://www.utdallas.edu/nserl/)

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The laboratory is divided into six sections as shown in Figure 1: **the wet chemistry area** (in blue), **the characterization area** (in purple, 2 zones), **the ultra high vacuum (UHV) area** (in green), **the corrosive gas area** (in red), a **machine shop area**, and a **Linear equipment room** (LER, in yellow). For safety purposes, the use of corrosive gases is restricted to a specific alcove, with a special exhaust and gas sensors (H\textsubscript{2}/D\textsubscript{2}, Cl\textsubscript{2}).

The LER is used for storage purposes and to house equipment like chillers, burn box, gas cabinets, compressors and mechanical pumps. All the main distribution of house gas (compressed dry air, N\textsubscript{2}), liquids (D.I. water, chilled water, hot water) and electricity go through that area and are then redistributed into the lab.
2 Wet chemistry facilities

The infrastructure of the lab includes two chemical preparation rooms (Figure 3, top) each one equipped with two fume hoods and a high purity de-ionized water polishers fed by high quality NSERL building DI water.

In prep. Room #1:
- Hood #1 is used for hydrofluoric acid or piranha solution cleaning purposes.
- Hood #2 is used for MOF (Metal Organic Framework) synthesis\(^1-^5\).

In prep. Room #2:
- The hoods are equipped with schlenk lines connected to vacuum scroll pumps. Gas cylinders of \(N_2\) and \(Ar\), located in between the two hoods, feed research grade purity gas into the schlenk lines for controlled-atmosphere functionalization chemistry.
- Hood #3 is used for graphene oxide synthesis\(^6-^10\).
- Hood #4 is used to functionalize oxide-free silicon surfaces\(^11-^15\).

In addition, the lab houses two glove boxes for controlled environment chemistry. A M-Braun dual glove box (Figure 4, top), in which the atmosphere is kept at a level of oxygen and water below 0.1 ppm, is used for chemical functionalization in anhydrous atmosphere\(^16\). Surface chemistry of sensitive species can be directly performed in the “Preparation” side (left) and the samples then transferred to the IR characterization side without being exposed to atmosphere. Acquisition of IR spectra under such conditions is greatly facilitated due to the low water vapor concentration, that is generally much higher in nitrogen-purged systems such as the small glove box shown at the bottom of figure 4.
3 Characterization facilities

Figure 5: In addition to optical probes dedicated to in-situ studies, the lab is equipped with equipment for ex-situ characterization:
1) SDT Q600 TA Instrument simultaneous TGA/DSC,
2) Woolam spectroscopic ellipsometer (193-1000 nm),
3) Rame-Hart Contact Angle Goniometer,
4) Veeco Dimension 3100 atomic force microscope,
5) Thermo Nicolet micro and macro Almega XR Raman spectrometer,
6) Horiba Jobin Yvon UVISEL spectroscopic ellipsometer (190-2000 nm),
7) BASi Controlled Growth Mercury Electrode.

The SDT Q600 provides simultaneous measurement of weight change (TGA) and true differential heat flow (DSC) on the same sample from ambient to 1,500 °C. It features a field-proven horizontal dual beam design with automatic beam growth compensation, and the ability to analyze two TGA samples simultaneously. DSC heat flow data is dynamically normalized using the instantaneous sample weight at any given temperature.

The Woolam spectroscopic ellipsometer (193-1000 nm) is used for in-situ and ex-situ measurements. Special ports have been added to the ALD reactors #1, #2, and #3 (See figure 7) to allow in-situ simultaneous IR/ellipsometry measurements in between two ALD cycles, without need of sample rotation/displacement.

Our Ramé-Hart Model 250 Goniometer/Tensiometer is a powerful tool for measuring contact angle, surface energy, surface tension, interfacial tension, and surface dilatational elasticity and viscosity. This system includes the DROPimage Advanced software as well as a fiber optic illuminator, 3-axis specimen stage with leveling, and a high-speed digital camera connected to the PC. Our set-up includes also an automated dispensing system allowing reproducibility with high control of drop sizes.
The Vecco Dimension 3100 atomic force microscope is the perfect tool to scan surface morphologies at the nanoscale. Enclosed in the cover of the anti-vibration table, the noise level is reduced to its absolute minimum, which ensures very high quality AFM images\(^{13,17}\).

Our Almega XR Raman setup is equipped with an Olympus microscope that allows to perform spectroscopic measurements with high spatial resolution. This feature had proved to be helpful in mapping various inhomogeneous samples, as well as certain nanostructured materials. For instance, in our studies on Ge nanowires we used this feature to spatially probe nanowires dispersed on glass and Si surfaces. By comparing our data at different spots, we insured that each measurement only involved a single nanowire. This highly simplified our work with data analysis related to the phonon confinement in nanostructured materials\(^1\). With its add-ons, such as the Linkam variable temperature stage (temperature can be varied from -196°C to 600°C), this equipment was useful in our studies of N\(_2\) and CO\(_2\) gas adsorption in metal-organic frameworks\(^2,18\) as a function of temperature in these novel materials\(^2\).

Related publications:

Our Jobin-Yvon ellipsometer allows measurements in a wide spectral range, from 0.6 eV to 7 eV. Spectroscopic ellipsometry is a useful tool for systematic studies of optical properties of thin films. In our group, we use ellipsometry as a standard tool for characterization of ALD-deposited thin films as well as thin organic layers. Other interesting applications include research on nanostructured materials: for example, from cross-referenced analysis involving AFM and ellipsometry, we deduce optical and structural properties of gold nanoparticles that are attached to silicon surfaces using various organic linker groups\(^3\).

The BASi Controlled Growth Mercury Electrode is a valuable tool for certain applications due to its high overpotential for hydrogen ion reduction and the high reproducibility of the electrode surface. The mercury drop is deposited a series of pulses that open a capillary valve. The number of pulses, their duration, and their frequency are either electronically or manually controlled, providing great flexibility in both the drop size and its rate of growth. In our laboratory, this tool is extremely valuable for electrical measurements on organic monolayer\(^13\) due to the possible soft contact induced by the mercury contact, especially knowing that evaporation of metals cannot be used because of damage to the organic monolayer.

### 4 High and Ultra high vacuum equipment:

![Figure 2: Photograph of the lab showing the UHV area. A hanging structure (10 feet from the floor) is used to support and distribute all water pipes, gas lines and electrical outlets to the various vacuum chambers.](image-url)
4.1 Atomic layer deposition (ALD) facility

The first generation of ALD reactors (ALD #4 and #5 on figure 2) were initially designed for in situ IR only. They can accommodate two precursor bubblers, one in a furnace and the second one kept at room temperature. The IR windows are protected by MDC 1.5” port gate valves whose bodies are directly welded onto the ALD reactor with the actual window attached on one side. The ALD valves are computer-controlled through a LabView program. They are also connected to different gas lines delivering specialty gas from cylinders (e.g., chlorine, ammonia and oxygen), or from specific production gas equipment (e.g., ozone generator, Nitrogen purifier).

The three second-generation ALD reactors (ALD #1, #2 and #3 on figure 3) are equipped with in-situ IR spectroscopy (Nicolet 6700 FTIR Interferometer), mass spectrometry (MKS Vision 1000-CTM), spectroscopic ellipsometry (Woolam M2000D ellipsometer (193–1000 nm), and can in addition accommodate a quartz crystal monitor. The multiple gas inlets of each ALD reactor can be used for 3 metal precursors and 4 gas lines, all controlled by ALD valves (Swagelok Diaphragm ALD valves). The N₂ purge gas used during the ALD process is purified through an Oxy-Gon 120 nitrogen purification furnace (O₂ concentration < 1 ppb).

Those home-built ALD reactors are equipped with a Pfeiffer turbomolecular pump capable of achieving pressures down to 10⁻⁹ Torr. The reactors are connected to a Nicolet 6700 FT-IR spectrometer, giving the system the capability of in-situ surface analysis in transmission mode. All precursors lines are made of stainless steel tubing. High purity N₂ pure gas is used to prevent cross contamination and to remove by-products from the chemical reactions. By interrupting the half-cycle, the growth mechanism is monitored after each gas exposure. This system provides information on the surface composition and termination during the initial growth cycles. Those equipments makes possible to study the oxide reduction on Group V elements (As₂O₃, As₂O₅, InPO₄, In(PO₃)₃, P₂O₅, etc.) upon exposure of TMA. One of those systems is used to understand the surface chemistry during the growth of Al₂O₃ on different chemically prepared surfaces of InP(100) and GaAs(100).
4.2 UHV cluster with in situ characterization (LEIS, XPS, IR) and plasma chambers

A new cluster tool is being finalized. It incorporates Low Energy Ion Scattering (Q-Tac LEIS from IonTOF), a Physical Electronics (5600) X-Ray photoelectron spectrometer, and a growth chamber with in-situ IR spectroscopy. The LEIS and XPS are already operational, having been tested with borrowed equipment. The growth chamber, under manufacturing, has been designed to be equipped with a remote plasma source (PCF-RF SPECS), an ion sputter gun (Omicron) and a metal effusion sources (EFM3, Omicron). This preparation chamber will be used to chemically modify metallic or semiconductor surfaces by either ALD/CVD or physical deposition and to study surface chemistry in situ. This cluster will be connected to two UHV chambers equipped for in situ IR spectroscopy in both reflection and transmission modes, dedicated to surface modification by direct and remote plasma.

Figure 8: Schematic of the future cluster combining XPS, LEIS and FT-IR for characterization, and Plasma (remote in UHV #3 and direct in UHV #4), ALD-CVD in UHV #8, for sample preparation.

4.3 Ultra High Vacuum Chambers

Our facility includes seven Ultra High Vacuum (UHV) chambers, all interfaced to FTIR spectrometers. Two UHV chambers are equipped with Low Energy Electron Diffraction (LEED), Auger Electron Spectrometers (AES), Temperature Programmed Desorption (TPD), Mass spectrometers, IR windows, evaporators, W filaments to crack hydrogen, metal effusion sources, sputter guns. They are both equipped with manipulators mounted on XYZ differentially pumped stages, with cooling (77 K) and heating (2000 K). One chamber (UHV #1) is specifically designed for grazing incidence IR spectroscopy and currently used to study metal surfaces. The other chamber (UHV #2) features a load lock with an internal chamber to perform MOCVD, to prepare for instance III-V surfaces with appropriate stoichiometry (i.e. selected reconstructions).

A second set of UHV chambers also sharing a FT-IR spectrometer is shown Fig. 7.b. UHV #3 accommodates both in situ IR in transmission and reflection modes, and is dedicated to surface modification with plasma by indirect exposure which makes it possible to control and select the species (radicals, electrons, ions) interacting with the surface. The second chamber (UHV #4) already manufactured but not yet installed, will be used for direct plasma treatment of surfaces at pressure in the torr range. Both chambers are equipped with manipulators mounted on XYZ differentially pumped stages, with cooling (77 K) and heating (2000 K) capabilities.

Three smaller UHV chambers are designed for IR in transmission mode only. One is used for CVD, the second one for physical deposition and the third one for remote plasma treatment. All chambers are equipped with heating (2000 K) capabilities, but only the CVD chamber allows cooling down to 173 K.
**UHV chamber #1:**

This UHV chamber is used to investigate the reaction mechanisms for hydrogen storage in complex metal hydrides that are being considered for hydrogen storage. Here we study the interaction of hydrogen with single crystal Aluminum surfaces. The system is equipped with two 500 l.s⁻¹ ion pumps in order to recover as fast as possible the very low pressure below 2x10⁻¹⁰ Torr in less than 10 minutes after H exposures. This is indeed critical to maintain clean the very oxygen reactive Al surface. Several characterization tools are mounted on that surface science UHV chamber: AES, RGA, QCM and LEED. Figure 9 presents rear view of the system, with the custom made gas manifold used to ensure control and purity of the different gases used for our research on Complex Metal Hydrides for Hydrogen storage.

**UHV chamber #2:**

This chamber can be set up for in-situ IR spectroscopy in transmission, reflection, or multiple internal reflection. The sample holder is mounted on a XYZ stage. Samples can be heated up to 1200°C by resistive annealing and cooled down to -180°C using liquid nitrogen. The Sample temperature is measure by a K-type thermocouples spot-welded on the Ta clips in direct contact with a sample edge. That chamber is equipped with RGA 300 amu, several gas lines connected to leak valves, LEED and sputter gun.
**UHV chambers #3 and #4:**

Those two UHV chamber share the same FT-IR spectrometer, leaving accessible the main compartment. With all the related electronic devices mounted on the table frame, this complete system can be easily moved to any other location in the lab.

![Figure 12: UHV chambers #3 (right) and #4 (left). Still under construction, those two chambers will be part of the UHV cluster described in section 5.](image)

**UHV #3:** This UHV chamber is integrated with IR spectroscopy. The surface interaction of gas adsorbates with the sample inside can be monitored by infrared spectroscopy in the temperature range of liquid nitrogen temperature to hundreds of degree. Electrical connections are incorporated for electrical characterization of samples under high vacuum, over a wide range of temperatures, and also as a response to gas exposure. This chamber can be equipped with a remote plasma source. Particles (ion, electron, radical, etc.) interacting with the sample can be introduced.

**UHV #4:** This UHV chamber is currently under construction and will be used for direct plasma-induced modification of silicon substrates. The surface modification is monitored by infrared spectroscopy in a double transmission mode at an incidence of 80 deg off normal. The flange supporting the exit KBr windows has been specially design to also allow direct transmission from normal incidence to Brewster angle (74 deg). The sample holder is mounted on an XYZ stage. The sample can be annealed up to 1200°C by resistive heating and cooled down to -180°C using liquid Nitrogen. The sample temperature is measured by a K-type thermocouple spot-welded on a Tantalum clips in direct contact with a sample edge.

**UHV chamber #5:**

This small UHV chamber (2x10^{-10} Torr) is used for in situ FT-IR in transmission mode. The UHV is achieved by a 270 l.s^{-1} Pfeiffer turbo pump associated with a Drytel 1055C dry pump (drag pump plus membrane pump). This system is currently used to study the epitaxial growth of silicon and/or germanium on silicon substrates oriented (100) by CVD of Disilane (Si2H6) and/or Digermane (Ge2H6) exposure. The samples can be annealed by resistive heating to ~1000°C, and cooled down to -120°C using liquid Nitrogen.

![Figure 13: UHV chamber #5. The UHV reactor is enclosed into an Aluminum box continuously purged with N2 gas. In that Al box are also located the parabolic and ellipsoidal mirror and the IR detector. Pumps, vacuum gauges and gas inlets are out of the box, below the table.](image)
UHV Chambers #6 and #7:

UHV #6
This small UHV chamber has been used to study Aluminum oxidation on CuO substrate. This system will be rebuilt shortly on the frame supporting the UHV chamber #7, as shown on figure 14. The two chambers will be connected to the same FT-IR spectrometer. This system will be setup up for IR studies in transmission mode from normal to Brewster incidence angle. An EFM 3 (Omicron) e-beam evaporator for physical deposition can be mounted on the extension facing down by 30 deg located on the right of this UHV reactor. The sample holder holds a quartz crystal balance to monitor the deposition rate during physical deposition. The sample can be heated by resistive annealing. Cooling capabilities are planned for the future. The chamber will be pump down by a Pfeiffer 270ls⁻¹ turbo pump.

UHV #7
In the remote plasma chamber, we are capable to reach to pressure down 10⁻⁹ Torr with using Pfeiffer turbo molecular pump. Our reactor is homemade and is also connected to a FTIR spectrometer for basic characterization of our sample inside the reactor. We can produce plasmas using most gases including reactive gases such as O₂, N₂, and H₂. The plasma is water-cooled. The most important feature of this system is to control atom fluxes with controlling the tuning. Having RF Auto Tuning unit is controlled the inductively coupled plasma source. This instrument has been used to characterize SiCN and oxide films upon plasma modification.

5 Specific setups in FT-IR spectrometer main bench compartment

Enclosures to study surface processes under controlled environment are routinely used in the main compartment of our FT-IR spectrometers. We adapt commercial systems as well we design and construct very specific reactors, or use commercial systems such as three Specac high pressure- high temperature (HP-HT) IR cell one Janis PTSHI series cold refrigerator (CCR) system (liquid He). The HP-HT cells operate between 300 K and 1100 K for a pressure range 0-60 atm. They can accommodate both transmission and reflection geometries. In addition, we possess several homemade reactors adapted to very specific environmental experiments.

5.1 Corrosive gas applications

Glass reactor:

A quartz cell has been specifically designed to study chlorine reaction with H/Si surfaces. Customized glass to metal adapter have been designed to mount KBr windows on each side of the reactor, so that the cell fit in the main compartment of the FTIR spectrometer. This reactor is also used for the growth, annealing and characterization of SAMs of phosphonic acid on SiO₂ and the interaction of ethanol with H-Si(111) surfaces.
All aluminum reactor:

Figure 19: Custom-made all-aluminum reactors interfaced to IR spectrometers to study aggressive vapor phase processing of semiconductor and metal surfaces (e.g. XeF₂ etching). Sample holders have been built for transmission and reflection geometries, as well as gas phase spectroscopy.

This high Vacuum cell (10⁻⁷ Torr) has been originally developed for XeF₂ treatment of Si, SiO₂, Mo, MoO₃ surfaces. The cell entirely made of aluminum fits inside the main compartment of an FT-IR spectrometer. Different top flanges have been designed for transmission, gas phase analysis and reflection. Later, we used this setup in-situ FT-IR to study fluorination of Al surface using XeF₂ gas. Since the resulting fluorinated aluminum surfaces are very hydrophilic, we studied the attachment of self-assembled monolayer (SAM) to AlFx surfaces, and verified the bonding mechanism between the SAM and the surface.

5.2 Non-corrosive gas applications

Figure 20: Experimental set-up for direct resistive heating of semiconductors the Si substrates showing a FT-IR spectrometer with the annealing chamber placed into the sample compartment. The reactor is pumped down by a vacuum Drytel 1055C pump to a base pressure of 10⁻⁵ Torr.

Annealing of Graphene Oxide samples on clean SiO₂/Si substrates is achieved by direct resistive heating of the Si substrates in a custom-made Aluminum reactor as shown in Fig. 20. The enclosure, connected to a vacuum pump, fits inside the main compartment of a spectrometer. The experiment is performed in-situ (in vacuum) and the experimental chamber is evacuated (10⁻³-10⁻⁴ Torr) to minimize environmental effects.

Inside the chamber, the sample holder is fixed so that the substrate is well-positioned. The substrate is tightened from the ends between two homemade Tantalum clips to allow resistive heating. The temperature is monitored by a K-type thermocouple spot-welded to a Tantalum-made clip attached to the sample edge. The samples are heated using 6010A DC Power Supply (0-200V/ 0-17A, 1000 W, Hewlett. Packard) operated in a current-controlled mode and the temperature is maintained constant using a computer-controlled Eurotherm DPI.

Figure 21: HP-HT cell installed in the main compartment of a FT-IR spectrometer. Special adapters have been designed and machined in Al6061 to ensure a perfect N₂ purge of the system, so the water, hydrocarbon and CO₂ gas level out of the cell is kept constant. All gas lines are made of 316 stainless steel tubing, ¼” OD.

The HP-HT cell shown on figure 21 is being used to study the water vapor interaction with prototypical MOFs materials and structural change upon hydration process. In our setup, a high-pressure cell has been installed into ThermoNicolet interferometer. The cell is connected to different gas lines [CO₂, CH₄, D₂O] and vacuum line for evacuation. Therefore the sample can be exposed to different gases in a well controlled environment at temperature varying from room temperature up to 800°C.
Two others HP-HT cells (See figure 22) have been installed inside the main compartment of FT-IR spectrometers and are currently being used to study H\textsubscript{2} interaction with metal organic framework materials (MOF). The MOF materials are pressed onto a KBr pellet and mounted inside the cell. The cell can be used to pressures up to 60 bars. Because of the low adsorption capacities of MOFs at room temperature we need to use high pressures to increase the loading. We have studied several MOFs\textsuperscript{2,3} for hydrogen storage and CO\textsubscript{2} capture.

![Figure 22: High-pressure high-temperature cell installed in the main compartment of a FT-IR spectrometer. Special adapters have been designed and machined in Al6061 to ensure a perfect N\textsubscript{2} purge of the system, so the water, hydrocarbon and CO\textsubscript{2} gas level out of the cell is kept constant.](image)

To study the mechanisms of gas adsorption such as H\textsubscript{2} at low temperatures, we utilize a Janis PTSHI series cold refrigerator (CCR) system (See figure 23). The system uses the compression of helium to reach very low temperatures \textasciitilde 5K. The IR measurements in this system are done in transmission to pressures up to \textasciitilde 1 atmosphere. Using IR spectroscopy we are able to get information about the kinetics of adsorption of H\textsubscript{2} in MOFs. We have studied\textsuperscript{1} adsorption of H\textsubscript{2} in MOF-74 at room and low temperatures.

![Figure 23: Janis PTSHI series cold refrigerator (CCR) system installed in the main compartment of an FT-IR spectrometer. A crane has been designed and built to ease the sample loading. Only the bottom part holding the IR windows is attached to the spectrometer.](image)
6 General equipment
7 Machine shop

Our lab’s machine shop is equipped with several hand tools like drill, grinder, saws, threat bits and dies, all sets of wrenches and screw drivers plus other miscellaneous tools. In addition, we have a drill press and a lathe suitable for small jobs that can be realized by each group member, after being trained.

8 Safety

Safety is a priority concern for every member of the group. The lab provides gloves, lab coats and safety goggles for chemistry, heat gloves for operating the different furnaces, and shield and gloves for liquid Nitrogen manipulation. Gas sensors for all potentially dangerous gases including H₂ are located in the lab as shown on figure 28c. Specific exhaust lines are connected to a Burn box to neutralize all toxic gases (reactants and products used for ALD, CVD and other vapor phase processes). The burn box is located in the LER, as shown in figure 28a. All dangerous gases, including H₂ are stored in explosion-proof gas cabinets also located in the LER (Fig 28b). A first aid kit, a shower and several eyes cleaners, are kept in good working conditions. All MSDS forms are continuously updated and located in the lab. Calcium gluconate tubes, available in different locations (one per prep room, plus one in the main lab), are regularly replaced before expiration.
9 Back Stage: L.E.R.

Figure 28: a: burn box; b: safety gas cabinets; a: Recirculating water chiller; b: DUO 65M primary pump, roughing all the turbo pumps of the different systems installed in the lab.

Figure 29: general view of the LER.
10 References


