2
Experimental Techniques and Instrumentation

The molecular devices have sub-nanometric scale. Fabrication and characterization of such devices require highly precise instruments. Scanning tunneling microscopy is one such instruments used for deposition and characterization of single molecules under ultra-high vacuum conditions. STM system makes use of highly sensitive piezoelectric materials along with quantum mechanical tunneling mechanism to sense tunneling current and then convert them to topographic image. The main utility of STM system is to study the morphology of surface and interfaces. There are several other components in STM like e-beam evaporator, crystal monitor, thermal/direct current heater, sputtering system, cryogenic chamber, tip-etching system, molecular beam pulsed valve source etc.

2.1 Theory of quantum tunneling

Unlike classical theory where electron is referred to as a particle, in quantum mechanics electron is considered as a wave and each electron is described by a wavefunction $\psi(z)$. This wavefunction is described by Schrodinger's equation.

$$-\frac{\hbar^2}{2m}\frac{d^2}{dz^2}\psi(z) + U(z)\psi(z) = E\psi(z) \tag{2.1}$$

Where ħ is normalized Planck's constant, m is electronic mass, U is potential energy of barrier and E is electronic energy. This equation lends us to two possible options. One is either the electronic energy (E) is greater than the potential barrier (U) or the potential barrier is greater than the electron energy. Let's consider the first case when E>U, the solution to equation 2.1 can be written as

$$\psi(z) = \psi(0)e^{\pm ikz}, \text{ where } k = \frac{\sqrt{2m(E-U)}}{\hbar} \tag{2.2}$$

k is also referred as decay constant

The energy of electron is usually greater than the potential barrier in metals/conductor therefore wavefunction is sinusoidal in metals while in case of vacuum/insulators the wavefunction is an exponentially decaying function as shown in fig 2.1(a). As it is clear that tunneling current mainly depends on applied bias and separation between tip and sample, one can calculate the quantum conductance of any material by bringing the tip near to the sample so that their orbitals start interacting as shown in fig 2.1(c). At z = z_e in fig 2.1(c) the tip is in single atom contact with the sample. For free electron in the metals the value of quantum conductance is $G_0 = \frac{e^2}{\pi\hbar} \approx 77.48\mu S$.

The Schrodinger's equation mentioned above is meant for time-independent single electron in one dimension only. While in reality researchers deal with many electrons problems therefore solving Schrodinger's equation will be very tedious. Hence semiclassical approximations like Wentzel-Kramers-Brilliouin (WKB) approximation is often used to solve general potential barrier problems. WKB approximation calculates the transmission coefficient (T) of electrons which tunnel through potential barrier to find out tunneling current.

$$T = e^{\left(-2\int_{z_1}^{z_2} k(z)dz\right)} \quad (2.3)$$

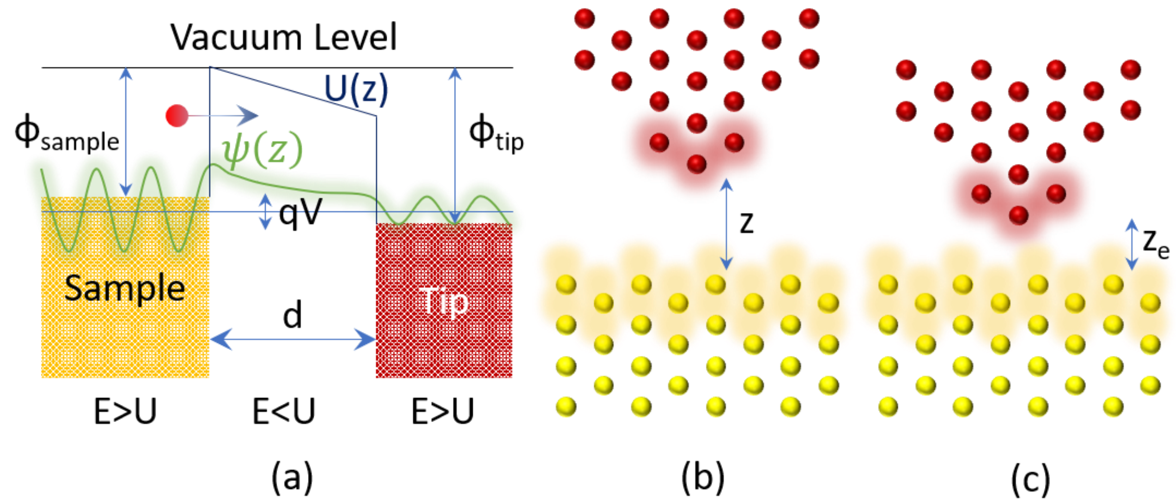


Fig 2.1 (a) Schematic representation of Energy diagram, (b) schematic representation of tip and sample at a tunneling distance of 'z', (c) a reduced tunneling distance 'z_e' between tip and substrate leads to Quantum conductance G_0 as single atom contact as in free electron metals.

Though WKB approximation provides information about transmission coefficient and the effect of distance on tunneling conductance but it didn't calculate the exact value of tunneling conductance at exact separation value between the tip and the sample. This information is provided by Landauer's theory by taking reference of experimentally calculatable separation between tip and sample as equivalent distance (z_e), which is the distance with zero net force. Landauer made two assumptions: first, electrodes can be described by 1-D free electron gas in an ideal square potential well and second, at $z = z_e$ current is ballistic.

2.2 Design of STM System

The STM was invented by Binnig and Rohrer in year 1981 and Gerber & Weibel helped Binnig & Rohrer in its implementation (Binnig et al., 1982a, b). The piezoelectric transducers are the pivotal components in the entire operation of STM. There are three mutually perpendicular piezoelectric sensors along x, y and z axis. A coarse positioner along with z-piezo help in automatic tip approach to substrate. The minimum step size of coarse positioner must be less than or equal to maximum expansion capacitance of piezo. The usual distance between tip and substrate at the instance of approach remains a fraction of nanometer length. Simple raster scanning is the procedure adopted to scan xy-plane. A sawtooth voltage signal at x-piezo will scan faster along x-axis and a voltage ramp signal at y-piezo will continuously rise the scanning tip along y-axis to capture the entire morphology in a frame.

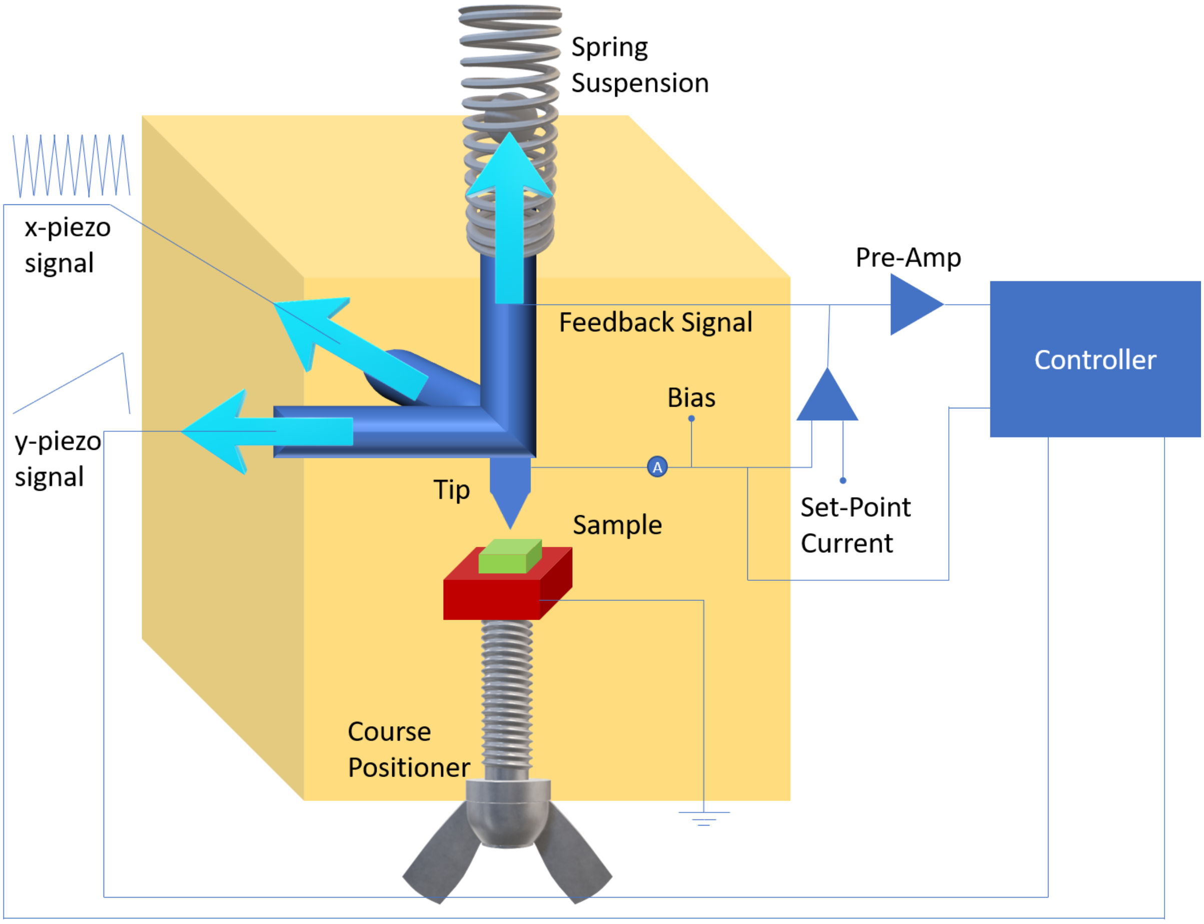


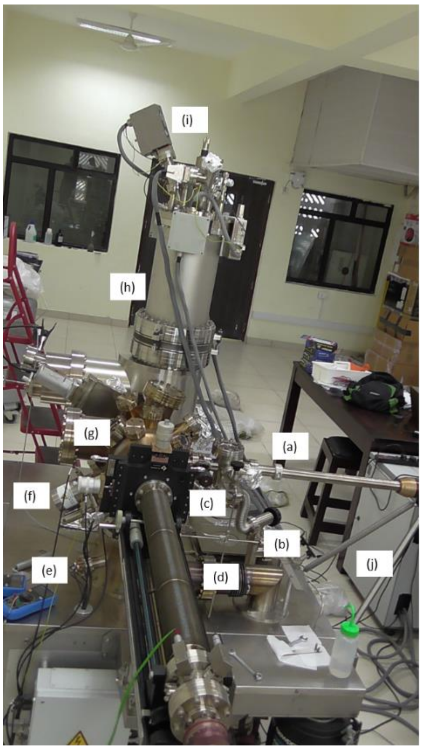
Fig. 2.2 Schematic representation of the inside design of scanning tunneling microscope.

Tunneling current observed at the tip has been used as negative feedback signal to the z-piezo to maintain constant current mode of operation. The constant current mode maintains the setpoint current value between tip and substrate irrespective of the roughness of the surface of substrate. If the real-time tunneling current is larger than the setpoint current value, then a voltage signal associated with z-piezo will retract the tip away from the substrate and similarly if real time tunneling current tends to be lesser than the setpoint current value because of surface morphology a voltage signal will try to push z-piezo and therefore the tip towards the substrate to maintain constant current. Apart from that vibration isolation is needed to achieve atomic resolution. UHV and low temperature (LT) conditions are also very important to neglect any external noise.

Fig. 2.2 gives a brief insight of the working principle of a scanning tunneling microscope. Highly sensitive piezoelectric sensors are placed orthogonal to each other around the tip to cover entire x-y plane and to capture the morphology of the surface in z-direction. The morphology of the surface is captured in the form of negative feedback current provided to the tip to maintain constant tunneling current at z-piezo. The x-piezo has been feed with a sawtooth signal and y-piezo has been feed with a ramp signal to scan a x-y plane. For auto approaching of tip coarse positioner is also provided. A spring suspension will help to damp the external vibrations.

2.3 Components in STM System for in-situ growth

The Low Temperature Scanning Tunneling Microscopy (LT-STM) that is used throughout is manufactured by OMICRON electronics GmbH (now Scienta Omicron). The system has many components like e-beam evaporator, crystal monitor, thermal/direct current heater, sputtering system, cryogenic chamber, tip-etching system, and molecular beam pulsed valve source associated with it for in-situ growth of materials.



(a) Load lock chamber
(b) Right angle valve
(c) Fast entry lock
(d) Manipulator
(e) Ion pump supply
(f) Argon sputtering
(g) Preparation chamber
(h) Cryostat chamber
(i) LT chamber control supply
(j) Matrix control system

(1) LT chamber
(2) Camera
(3) Ion gauge power supply
(4) E-beam evaporator
(5) Pneumatic valve
(6) Turbo
(7) Damping Legs
(8) Rough pump
(9) STM control Panel

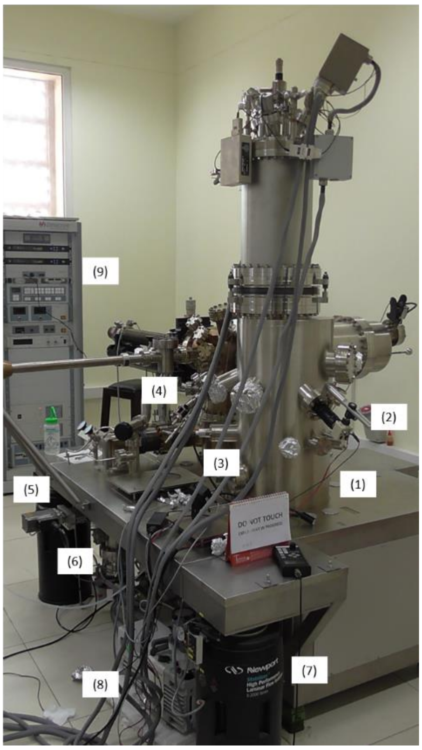


Fig 2.3 Front and back view of LT-STM system along with highlighted key components.

2.3.1 e-beam evaporator

The e-beam evaporator used in LT-STM has been manufactured by Focus GmbH. The evaporator has a flux monitor, a filament/thermocouple feedthrough and a high voltage (HV) feed-through along with cooling water connection and shutter actuator. The material which has to be evaporated will be filled in a crucible. The crucible is connected with a high voltage feedthrough by a rod at the end and it is electrically isolated from rest of the evaporation system. The front crucible is few millimeters away from a filament. As crucible approaches towards filament by external positioner electrons from filament start to move towards high voltage crucible. This will induce emission of electron beam from filament to crucible. When this electron beam hit the crucible, it will heat up the material inside crucible. The number of electrons induced from filament (emission current) can be controlled by separation between filament and crucible, voltage at crucible and filament current. Emission current is the key parameter to control the sublimation temperature at crucible. Sublimated material when pass through flux monitor induce flux current. From the flux current one can identify the evaporation of material. The sublimated material is then focused on substrate to deposit the material. This technique of material evaporation is highly precise and uniform layers of materials can be deposited on substrate.

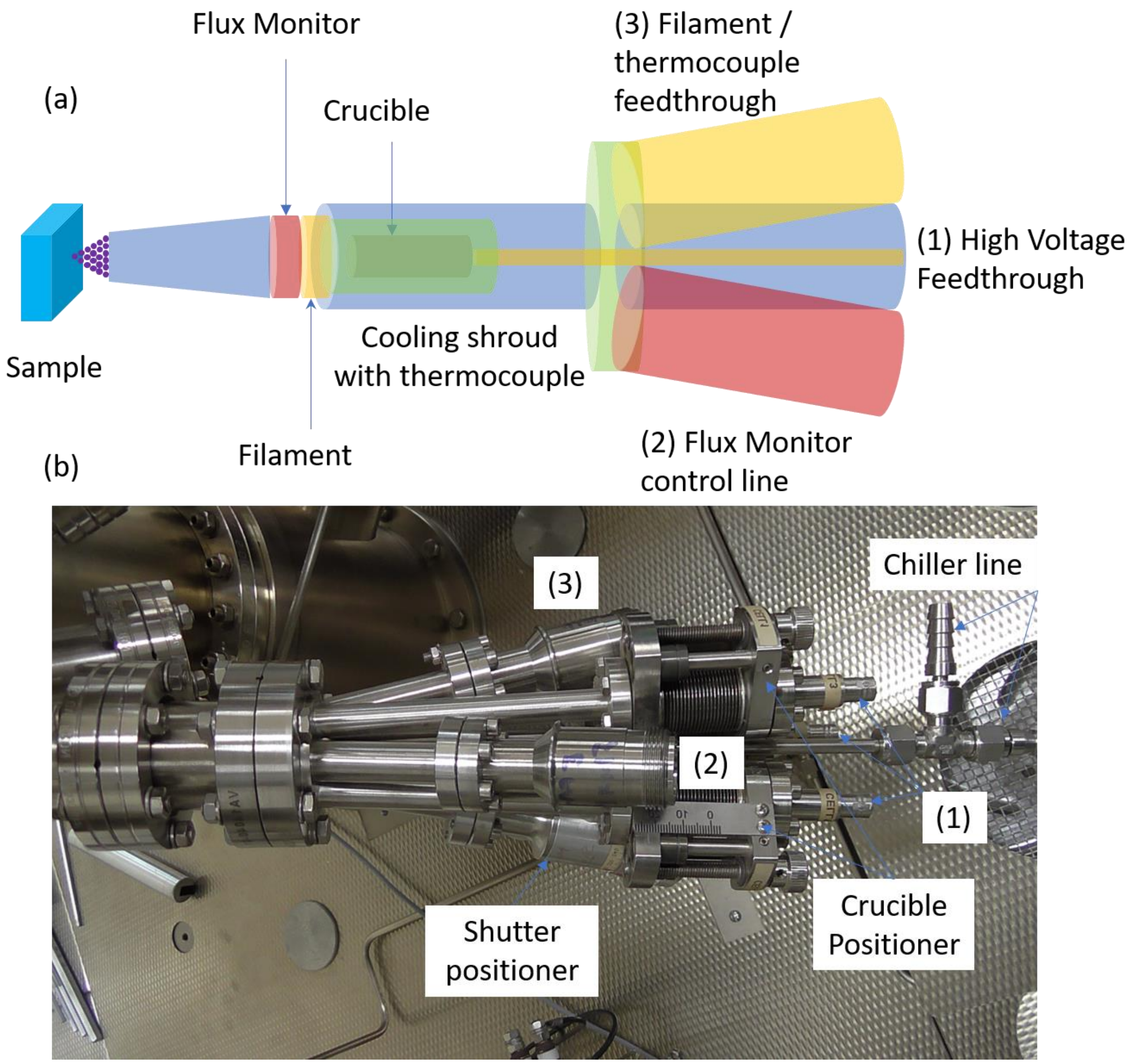


Fig 2.4 (a) Schematic representation of e-beam evaporator in STM system. (b) Picture of the EFM system with slots of three crucibles.

2.3.2 Crystal Monitor

Most commonly used crystal monitors are quartz based because of their piezoelectric nature. When an evaporated material deposits on quartz crystal it will induce current in the crystal. This current can be used to determine the thickness of the material deposited on the crystal monitor by normalizing some key parameters like density of the material, z-factor and tooling factor. Density of the material and z-factor are known to us for any particular material while tooling factor can be set to less than 100% if the sensor lies between e-beam evaporator and sample or it must be greater than 100% if sensor is placed beyond sample.

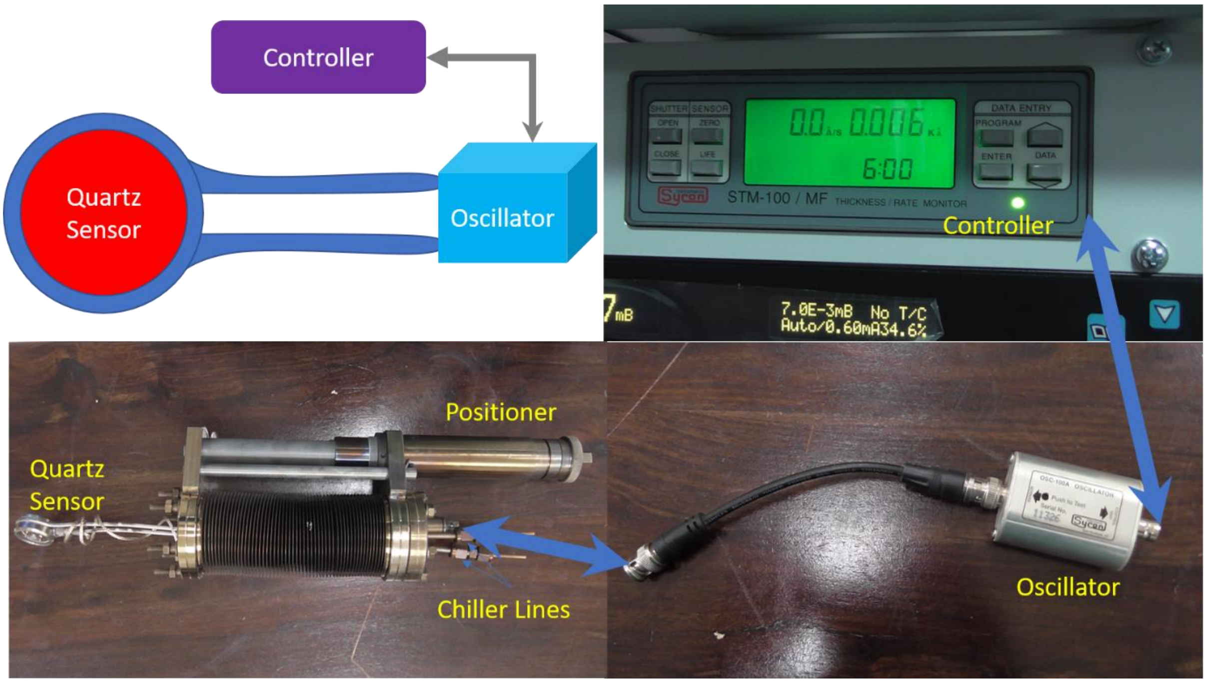


Fig 2.5 Schematic diagram and actual images of crystal monitor used in LT-STM system.

2.3.3 Thermal/Direct Current Heating

The LT-STM system is equipped with Pyrolytic Boron Nitride (PBN) coated thermal heater as well as direct current heater on manipulator. The PBN coating provides high thermal conductivity and anisotropy which can help to achieve very high temperature under UHV conditions. On the other hand, direct current heating needs direct current sample plate which isolate one side of the sample from rest of the place with the help of ceramic rings. Direct current heating is useful in semiconducting substrate like silicon only because their resistance is significantly higher than metals. The current induced heating helps semiconducting crystals like silicon to achieve very high temperature and therefore restructuring their surface upon cooling down. The rapid heating and cooling down (flashing) with the help of DC heater has also been practiced by experimentalist to achieve uniform surface. An attached thermocouple in manipulator provides exact value of temperature at any instance.

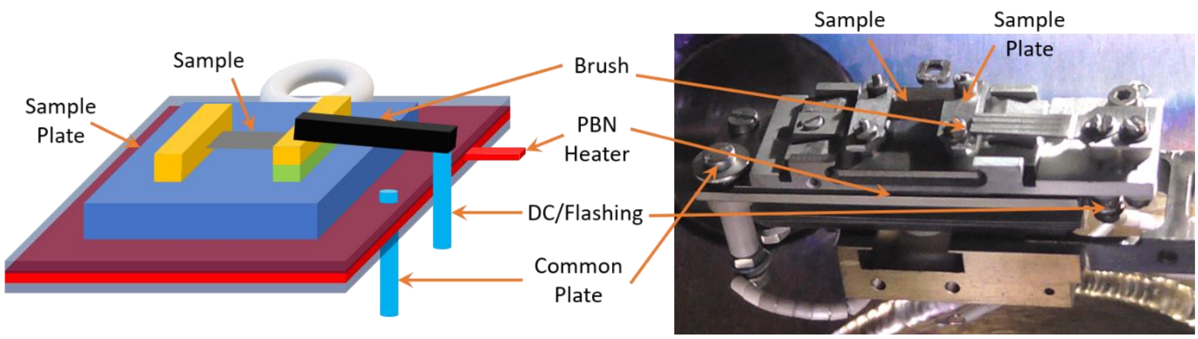


Fig 2.6 Schematic and real picture of a direct current heating place with silicon substrate mounted on manipulator.

2.3.4 RF Sputtering system

The argon ion sputtering system used in LT-STM is primarily aimed for cleaning of substrate by bombarding focused beam of argon ions on the sample. The operation of sputtering system is very straight forward. Argon gas is subject to pass into gas cell through controlled flow from inlet valve. Argon atoms then pass through a cathode plate and get ionized. Anode is used to accelerate the flow of argon ions in the presence of constant magnetic field. The argon ion beam then passes through focus plates which help to converge the beam on the substrate. This is a cold field emission process.

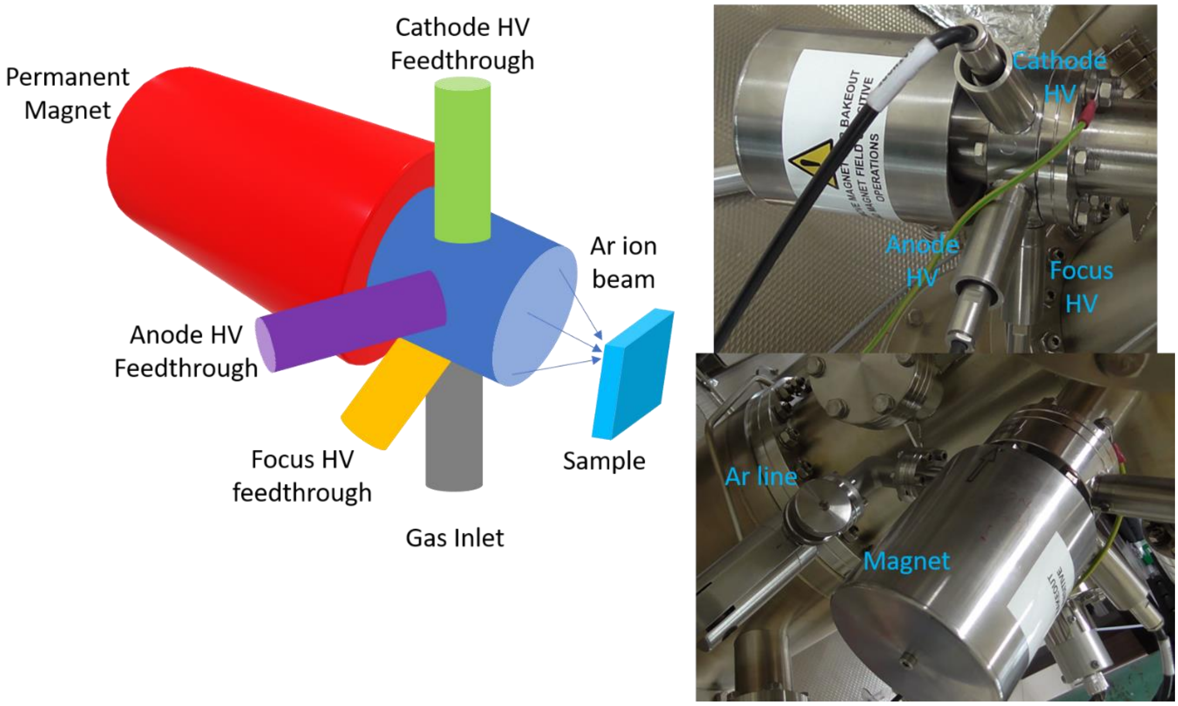


Fig 2.7 Schematic diagram of the argon ion sputtering system along with photographs of mounted system.

2.3.5 Cryogenic Chamber

To achieve low temperature the cryogenic chamber in LT-STM has one outer well for liquid nitrogen and one inner well for liquid helium. With liquid nitrogen 80K temperature can be reached while liquid helium can drag it down to 4K. The heat transfer is mainly dominated by conduction via connecting rods between cryostat and scanning stage. Liquid nitrogen can directly be transferred from Dewar to cryostat but transfer of liquid helium requires special accessories.

Schottky emission play crucial role at room temperature in quantum tunneling regime. Due to Schottky effect the potential barrier reduce by certain amount which in terms alter the scattering matrix parameters and thus the properties of material. Low temperature condition eliminates such effects and help us understand the quantum phenomenon of nano particles more discreetly.

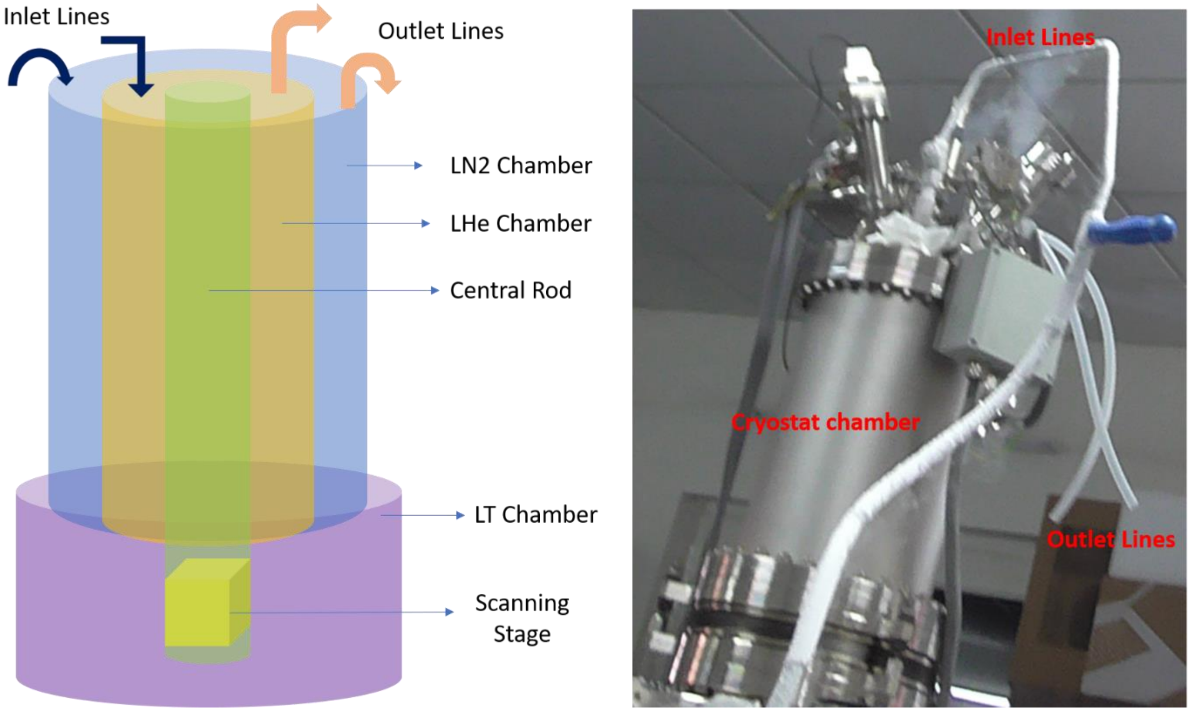


Fig 2.8 Schematic representation of cryostat and image of cryostat mounted on top of LT-STM while transferring liquid nitrogen from Dewar.

2.3.6 Tip-preparation tool

There are two types of tips used in the STM system. One is STM mode tip which can be mounted with Tungsten (W) wire as well as Platinum Iridium (Pt-Ir) wire and the other one is q plus sensor in which W-wire is glued on flexible quartz prong. STM mode tips can't be used in AFM while q plus AFM tip can perform in both STM mode and AFM mode.

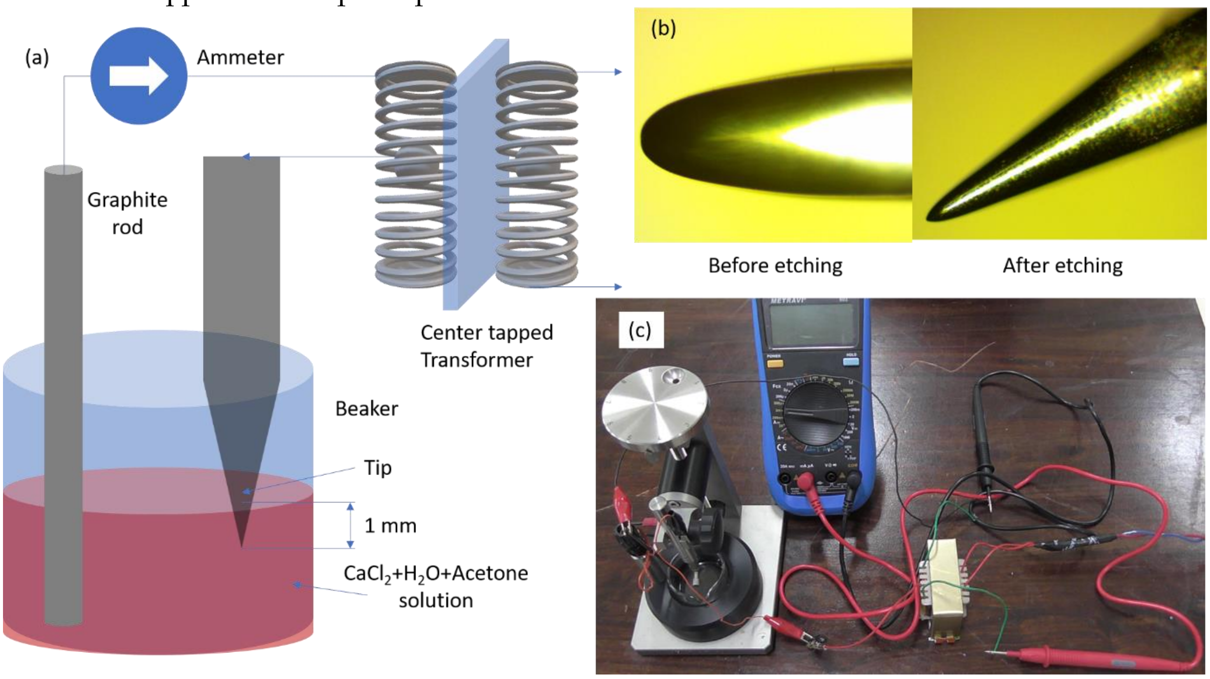


Fig 2.9 (a) Schematic diagram of electrochemical setup for Pt-Ir wire etching. (b) Microscopic images of Pt-Ir wire before and after etching. (c) Experimental setup for electrochemical etching.

Q plus tip can also partially be used in STM and AFM mode simultaneously. Pt-Ir tips with 70:30 ratio of Platinum and Iridium increase its strength 10 times as compared to pure platinum tip. Though sliced Pt-Ir wire may have atomic edge even after an inclined cut but electrochemical etching makes it further sharp. Procedure for etching of Pt-Ir tip and W-tip is slightly different. Electrochemical etching of W-tip requires NaOH solution and a ring-shaped electrode along with a function generator to produce desired electrical waveform to activate electrochemical reaction. While electrochemical etching of Pt-Ir wire requires aqueous solution of $CaCl_2$ and acetone and a graphite rode. A 12-0-12V center tapped transformer is an efficient and economical choice as compared to function generator for etching of Pt-Ir tip because transformer produces natural sinusoidal wave form at constant 50 Hz frequency.

An in-situ tip preparation tool is also attached to LT chamber of STM system to sharpen the STM tip under UHV conditions. The in-situ tip preparation unit is consisting of a filament wire which induces electron beam when a STM tip with high voltage feedthrough appears in its proximity. The sharpness of the tip can be controlled by HV between tip and filament, filament current and separation between filament and tip.

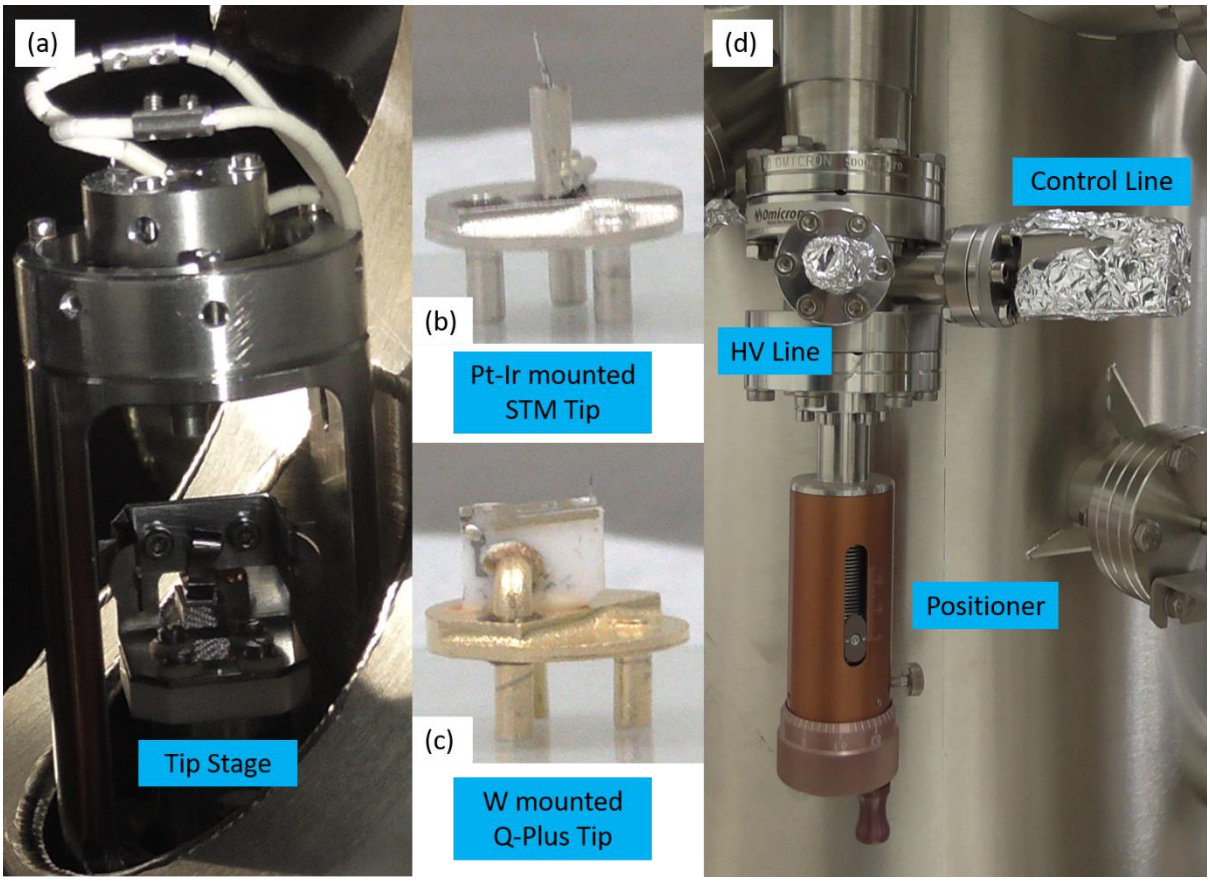
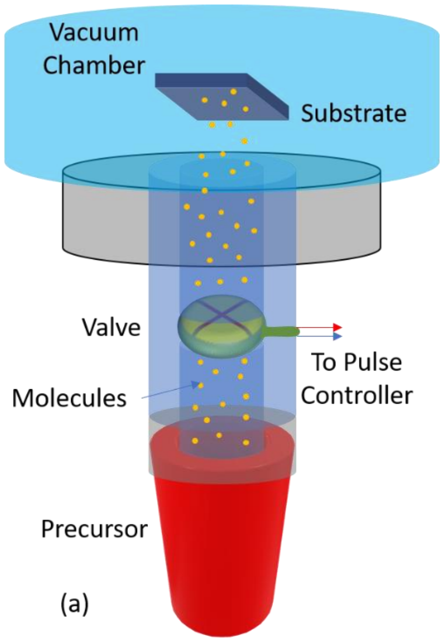


Fig 2.10 (a) Inner section of Tip preparation unit within LT chamber. (b) Pt-Ir Tip mounted on STM tip holder. (c) Tungsten tip glued on flexible quartz prong of Q Plus sensor. (d) Outer section of tip preparation tool.

2.3.7 Molecular beam pulsed valve source

The STM system has another unique feature for deposition of organic molecules or metal-oxides from their precursor to substrate by controlled opening/closing of pulsed valve. The pulse valve is a tiny mechanical valve controlled through electrical source. The mechanical valve opens only when a rated power signal appears across it.



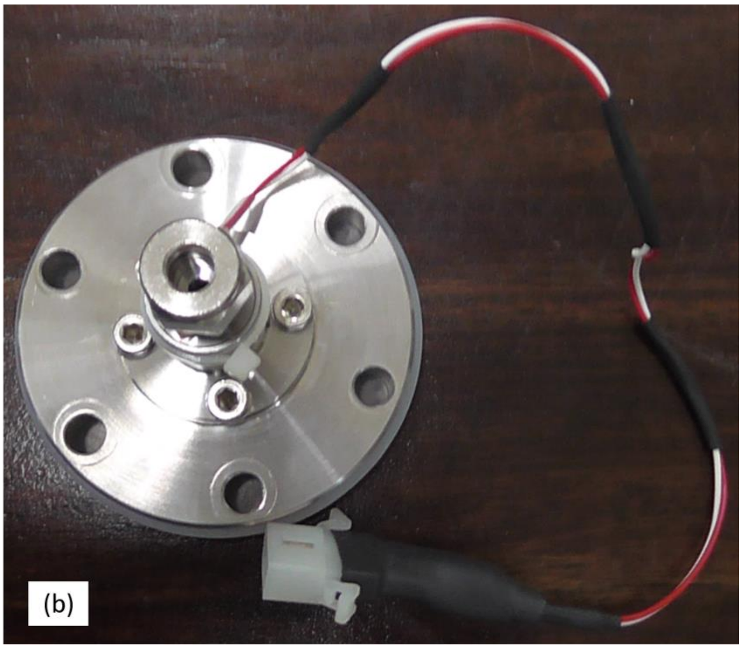


Fig 2.11 (a) Schematic diagram of deposition of molecule from precursor to substrate through pulse valve. (b) Image of pulse valve.

2.3.8 Ultra High Vacuum (UHV) Condition

Apart from temperature, vacuum also helps to get better surface resolution. Several mechanisms have been employed in STM system to achieve ultra-high vacuum (UHV) of the order of 10^{-11} mbar. Turbo & rotary pumps, ion pump, ion gauge, TSP, and whole system baking are some of the systems and procedures to accomplish, maintain and quantify the UHV conditions. The primal source of vacuum is combination of turbo and rough pump which can bring a change in pressure from 1 atm to 10^{-7} mbar. Turbo and rough (rotary) pump are connected through foreline with a pirani gauge installed somewhere in the foreline to measure the pressure. The pirani gauge is useful in measuring change of pressure from atmospheric to few millibar. Turbo pump is directly connected to load lock chamber (LLC) via right angle valve and to preparation chamber (PC) via a pneumatic valve as shown in fig 2.12(d). To bring down the pressure further from 10^{-7}mbar to 10^{-11}mbar ion getter pump (IGP) or simply ion pump will be required. An ion pump has high voltage across its anode and cathode of order of 6-7kV which is sufficient to ionize most of reactive gases. After ionization of gases a magnet beneath the electrodes trap the ionized molecules of the gas. Fig 2.12(a) gives the schematic diagram of a typical ion pump. To record such a low value of pressure ion gauge is used in mostly UHV instruments. In ion gauge, a thorium coated filament is used as hot electron ejector by passing certain amount of current through it. A cylindrical grid next to the filament as shown in fig 2.12 (b) helps electrons accelerate in the middle to ionize the gas molecules. The ionized molecules finally strike to ion collector wire and produce certain amount of current. This current is then used to determine the pressure inside the chamber. To maintain the constant pressure once UHV condition is reached, a titanium sublimation pump (TSP) is used. A typical schematic of a TSP is shown in fig 2.12(c) which has three Titanium filaments connected to one common rod. When a high current is passed through titanium filament sublimation of titanium atoms has been observed which is useful in maintaining the UHV condition as titanium has very high pumping speed for active gases.

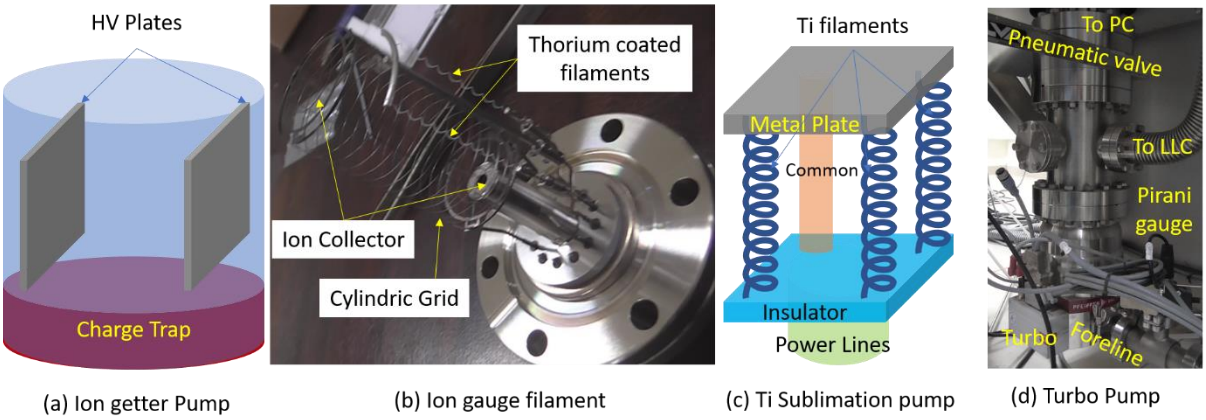


Fig 2.12 (a) Schematic diagram of an IGP pump. (b) Image of ion gauge. (c) Schematic diagram of Titanium sublimation pump and (d) image of turbo system connected in STM.

Another way of maintaining the UHV condition is baking the whole STM system at a constant temperature of 150°C for 3-4 days. Usually, this process is followed after the deposition and characterization of a material has been completed. All non-bakeable parts like camera, preamplifiers, connecting cables etc has been removed before baking and entire system is covered with walls. The long-time heating will push gas molecules to leave the chamber walls and ultimately, they will be sucked by turbo and rotary pump.

2.4 Device Characterization

There are two major characterization (surface morphology and electrical characterization) that can be performed with STM system. Surface morphology can be performed in both STM and AFM modes depending upon type of tip being used for scanning the surface. While electrical characterization can be performed by tunneling of current from tip to substrate through the molecule and also with the help of in-situ four probe system.

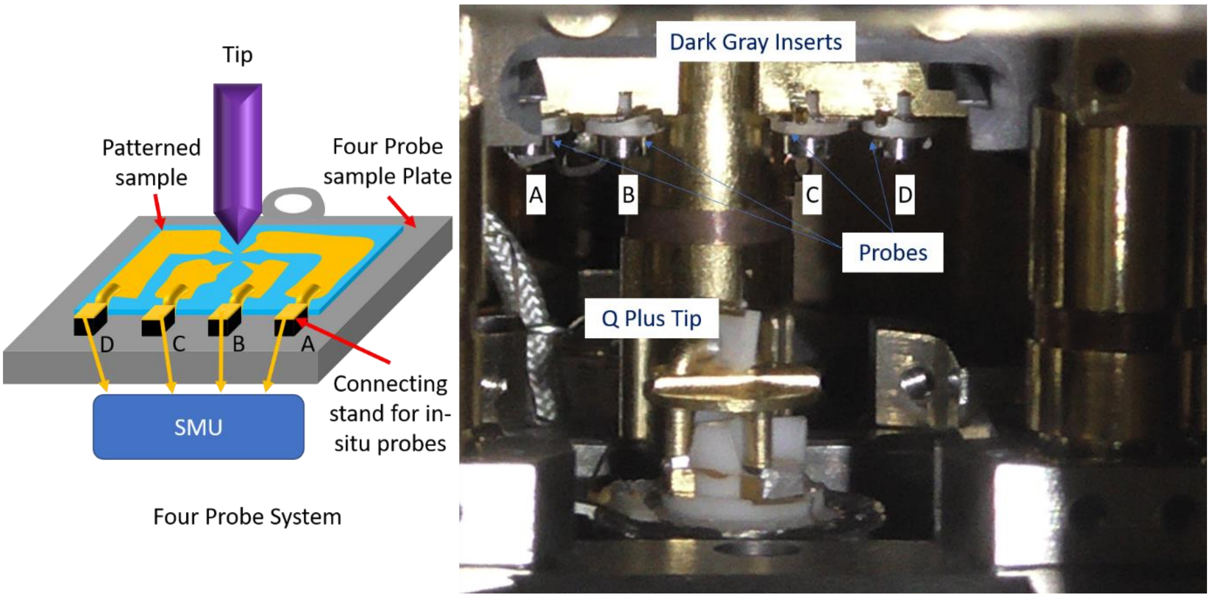


Fig 2.13 (a) Schematic representation of a four-probe sample plate (b) Image of four probes labeled from A-D inside scanning area.

Apart from that system can also evaluate magnetic and optical properties of the material. Electrical characterization of the material through four probe system requires prerequisite substrate pattern with high order of contact formation. Material can also be characterized by verity of external signals.

2.4.1 Data Acquisition

The LT-STM system by Omicron has Matrix hardware and software interface between Preamplifiers and computer system. The matrix hardware (control unit) consists of native boards, power input and legacy boards along with multiple input and output BNC ports. Native boards are further subdivided into master board and satellite board. The analogue data from pre-amplifiers is received at satellite boards and converted to digital signal. The digital signal then communicated with computer by master board. The legacy board helps in driving the STM system. It has piezo driver, course positioning board, analogue adapter board and serial bridge board.

The matrix software provides user interface with STM system. Software experiment section is also divided in two sections. One section is dedicated to STM operations only. In this mode STM tips are used for scanning the surface. Second section is meant for Q+ AFM operation. In this section both STM and AFM modes can be used independently as well as simultaneously. Q plus tip is used for surface scanning. Apart from both STM mode and AFM mode, atom manipulation is also feasible at low temperatures from one spot to another.

The data acquisition mechanism in STM can be compared with that of a digital camera in which entire frame is a combination of several pixels. In STM, tip stays at a point for a set amount for time (controllable) and then move to next point until it reaches at the end of the line and keep scanning in raster form. The number of lines per frame and number of points per line can be set before starting the project. Other controllable parameters are gap voltage between tip and substrate, current setpoint value, feedback loop gain and drift compensation. Data have been saved in the form of surface (Z) imaging and current (I) imaging. For electrical characterization three data acquisition modes are provided: V-mode, Z-mode, varied Z mode. During V-mode separation between tip and substrate remains constant. Current voltage (I-V) characteristic and conductance voltage plot can be studied with V-mode. In Z-mode, voltage remains constant and tunneling region can be identified by bringing tip closer to substrate. Current distance (I-Z) plot gives better idea of separation between tip and substrate as well as quantum conductance can be calculated with the help of I-Z plot. Varied Z mode is a combination of V-mode and Z-mode.

2.4.2 Data Analysis

Vernissage and SPIP are the two preinstalled software used for data analysis of STM data. Both softwares can read Z image and I image. Various Fourier transform analysis can further enhance the image quality. Line profiling in SPIP helps to calculate surface roughness as well as the number of layers stacked on one another. This information is very crucial in characterization of self-assembled multilayers of molecules. The condition of tip can also be evaluated by analyzing the surface morphology with SPIP. Vernissage is helpful in analyzing electrical characterization data like I-V and I-Z plots.