2
Experimental and Analytical Techniques

To successfully carry out research in the field of microelectronic fabrication, it is very important to select the appropriate and suitable experimental techniques for the device. Choice of a fabrication technique depends on various factors like ease of the method, overall cost, and reliability of final product whereas the choice of characterization technique depends on the physical parameter under test and the accuracy of the method used. Devices fabricated with a highly reliable method yield consistent results. Parameters extracted from the accurate data obtained from the suitable techniques provide insightful information about the device under test. This chapter will discuss some of the experimental and analytical techniques used in the research work.

2.1 SUBSTRATE CLEANING

The particular method for cleaning the substrates being discussed here is applicable to most substrates including glass, indium tin oxide (ITO) coated glass, and silicon [Vyas *et al.*, 2016]. In this method, the substrates are first submerged into the soap water and ultrasonicated. Soap cleans up the coarse impurities on the substrate such as oil, dirt and other impurities from previous processes, such as polishing of the silicon substrates. Often, in case of hard and brittle substrates, after cutting them, traces of glass dust stay on the substrates. To remove the glass dust and other such very small particles, *ultrasonication* is needed. Ultrasonication is a procedure in which an object is submerged in water (or any other cleansing liquid) and is subjected to ultrasonic pressure waves up to 40 kHz. The ultrasonicator used in the current study is DSA100-SK2-4.0L Ultrasonic cleaner from Phoenix instrument.

Figure 2.1: The DSA100-SK_2-4.0L Ultrasonic cleaner from Phoenix instrument used in the current study.

After the soap treatment, substrates are rinsed in de-ionized water (DI water or DI) to remove the remnants of soap, ultrasonicator may also be used in this step to achieve better cleaning. The previous step is repeated each time with fresh DI water until there are no soap bubbles visible. After cleaning with DI water, the substrates are ultrasonicated in acetone, DI water and then methanol for 15 minutes each. Cleaning with all three solvents mentioned above is repeated thrice, each time with fresh solvent. Due to the different ranges of solutes of these three solvents, this cleaning method proves to be very effective. After cleaning, the substrates are dried up in an oven at 70ºC for a few hours. Temperature and duration of drying can vary according to the requirements.

2.2 SPIN COATING

Spin coating is probably one of the simplest methods of fabricating thin layers of a given material. The spin coating is a thin film deposition technique in which the desired material, dissolved in a suitable volatile solvent, is applied over the substrate which is then spun at high speed [Birnie, 2004; Hall *et al.*, 1998]. While spinning, the solution gets spread out uniformly over the entire substrate and extra solution is thrown out with the help of centrifugal force acting outwards. Final thickness and quality of the film depend on many aspects such as rotational speed, the viscosity of the solution (which can be subject to the concentration), and volatility of the solvent. The higher the speed, the thinner the films are and higher the concentration of the solution the thicker the films are observed. However, the rate of thinning of the film further increases at high speed because of the higher interaction of air and the top surface of the solution spread over the substrate [Middleman, 1987].

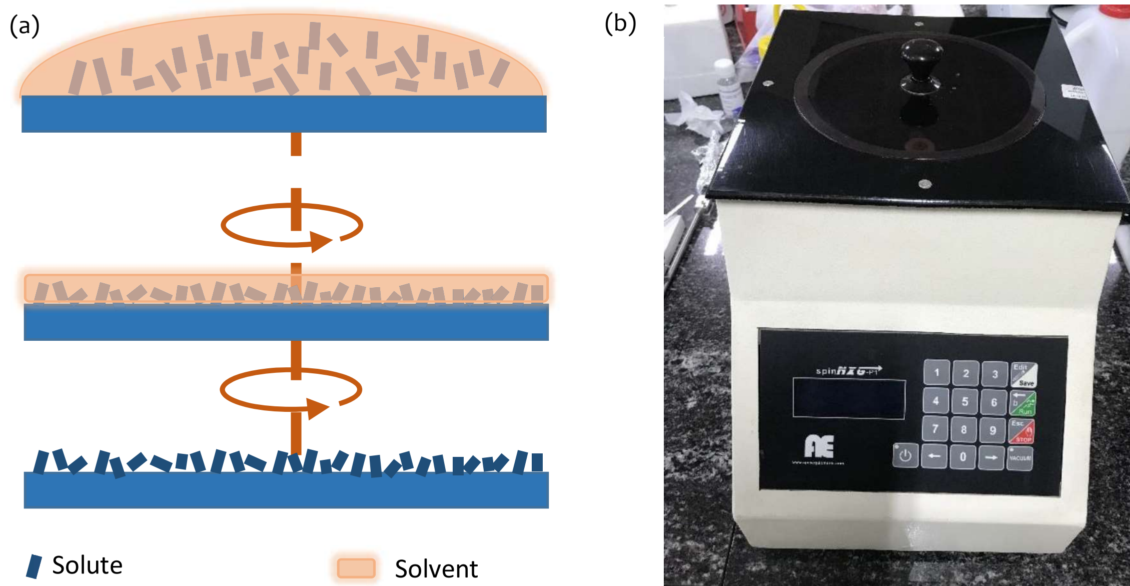


Figure 2.2: Spin coating: (a) Schematic diagram depicting spin coating process, (b) The spin coating system used in the current study - spinNXG-P1 from Apex Equipments.

The main advantage of the method is that it's a quick and easy method of producing good quality thin films of solution processable materials. The main disadvantage of spin coating in terms of film quality is that where highly oriented films are required, spin coating can result in films with rather poor orientation because of the high drying rates at the high speeds of rotation. Other disadvantages in terms of industrial viability are that there can be only one substrate

processed in one go, and also the wastage of solution is very high compared to the material actually coated on the substrate [Ossila, 2018]. The spin coating system used in this study is spinNXG-P1 from Apex Equipments as shown in figure 2.2(b). The films based on polymer-small molecule blend used in the current research were spin coated at 1000-7400 rpm speeds.

2.3 THERMAL EVAPORATION

Thermal evaporation is a very popular physical vapor deposition (PVD) technique. In thermal evaporation, a material is heated under high vacuum conditions till it starts evaporating and the vapors are collected at the substrate where they condense and form a thin film [Harsha, 2007]. The material is generally heated with a resistive filament or boat which is generally made of tungsten or alumina. In some cases, the material is put in a crucible and heated with the help of an electron beam. This method of evaporation is called e-beam evaporation. In thermal evaporation, the material is often kept vertically below the target substrate as shown in figure 2.3(a). The entire procedure takes place in a high vacuum (>10^{-6}mBar) chamber. A high vacuum in the chamber causes lowering of the boiling point of the molten material (often metal). A high vacuum in the chamber also reduces the mean free path for the vapors of the material, hence creating a straight path from source to target. Also, at this high temperature, there is a possibility that target material and/or heating boat or filament can get oxidized in the presence of air, which is prevented by having a vacuum in the process chamber.

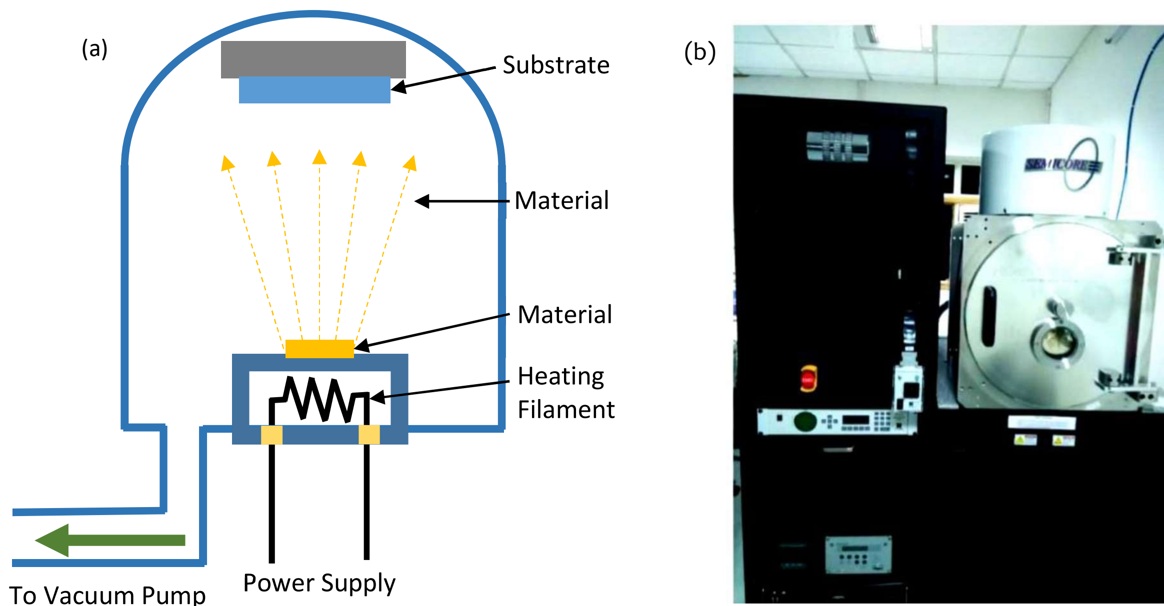


Figure 2.3 (a) Schematic diagram of a thermal evaporation system, (b) SC-Triaxis thermal evaporation system from Semicore used in experiments

The main application of thermal evaporation is in the coating of top contacts in electronic circuits. RF sputtering is another method by which the top contacts in the integrated electronic circuits are deposited. In case of organic semiconductors, thermal evaporation is most suitable for deposition of top metal contact because it involves low-intensity vapors which sit gently on top of active organic layer whereas, in case of RF sputtering, there are high energy metal ions which are crashed through the soft organic solid, damaging its structure. The disadvantage of thermal evaporation is the wastage of a large quantity of material because when the evaporation process

is carried out, not only the substrate but the entire process chamber gets coated with the evaporated material.

The final film thickness in thermal evaporation depends on the density of the material being deposited, the rate of evaporation (which can be controlled by the heating) and the duration for which evaporation is carried out. The thermal evaporation system used in the current research is SC-triaxis thermal and e-beam evaporation system from Semicore, is shown in figure 2.3(b).

2.4 SURFACE PROFILING

Surface profiling is a technique by which linear height – distance profile of a surface can be traced. It involves scanning of a surface in a straight line with a sharp stylus [Dong-Hyeok and Nahm-Gyoo, 2012; Euan, 1996]. Stylus is a probe with a very sharp tip. The stylus tip scans the surface along a line. The stylus is attached with a lever mounted on a stage which moves vertically as the stylus tip traces the crests and the trough on the surface as shown in figure 2.4(a). Stylus applies a very small force on the surface. A feedback loop measures the movement of the stylus and balances the amount of force to keep it constant. The change in the position of the stylus to keep the force to a pre-defined value is recorded which is used to construct the profile of the surface. Figure 2.4(a) shows the schematic of the surface profile measurement process. The resolution of measurement depends largely on the sharpness of the stylus tip. Sharper the tip, higher the resolution achieved in the measurement. Apart from the sharpness of the stylus, the speed of scan also affects the measurement. Surface profiling has a disadvantage – the scanning by sharp tip can cause damage to soft organic solid films. Also, the tip of the stylus can get contaminated by such films. A contaminated stylus causes an error in the measurement.

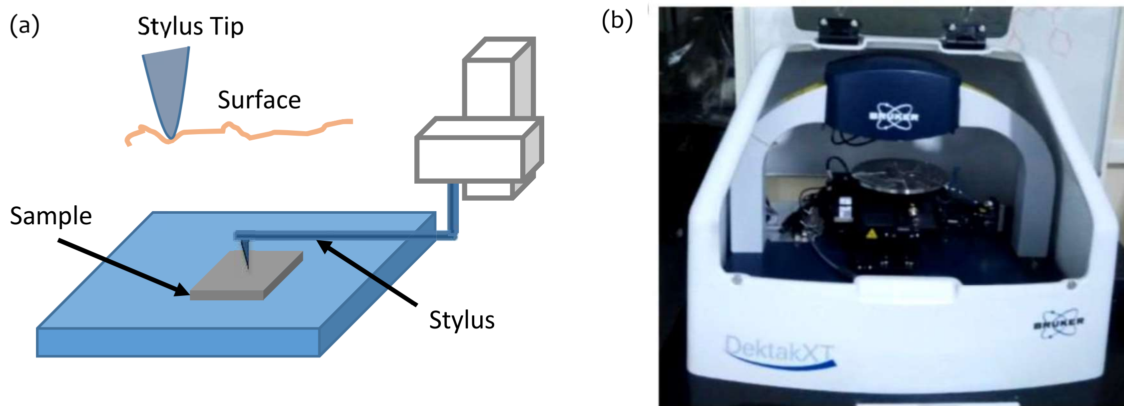


Figure 2.4: (a) A schematic diagram of a basic surface profiling scheme, (b) DektakXT surface profilo-meter system from Bruker used in measurements.

In the current research work, linear surface profilometry was used to find out the thickness of organic thin films. The instrument used for measurement was DekTak-XT surface profilometer by Bruker, as shown in figure 2.4(b). The radius of the stylus used was 2μm.

2.5 ATOMIC FORCE MICROSCOPY

Atomic force microscopy (AFM) is one of the most advanced microscopy techniques used today. The AFM technique is based on the inter-atomic forces that act between the AFM tip and the grains on the surface under test [Eaton and West, 2010]. It is possible to achieve atomic resolution with modern AFM techniques [Schimmel *et al.*, 1999]. AFM principally works in two modes – contact and non-contact mode [Park, 2018]. In non-contact mode, as the AFM tip is

brought close to the surface, the attraction force between the tip and the surface starts acting on the tip. The tip is connected to a cantilever, which starts oscillating according to its resonant frequency. While the surface is scanned, any pits or crest in the way causes the frequency of oscillation to change because of the change in the attraction forces. A feedback loop checks and balances this change of frequency, and the change in the vertical displacement of the mean position of the tip (z) is recorded which is used for the construction of the surface morphology. In contact mode, however, the tip is brought so close to the surface that the repulsive forces between the tip and the surface start acting on the tip, and if there is a force applied from the cantilever on the tip, the cantilever bends. The bend in the cantilever is measured and through a feedback loop, the applied force is kept constant. The change in the z is measured and the information is used to construct the profile of the surface.

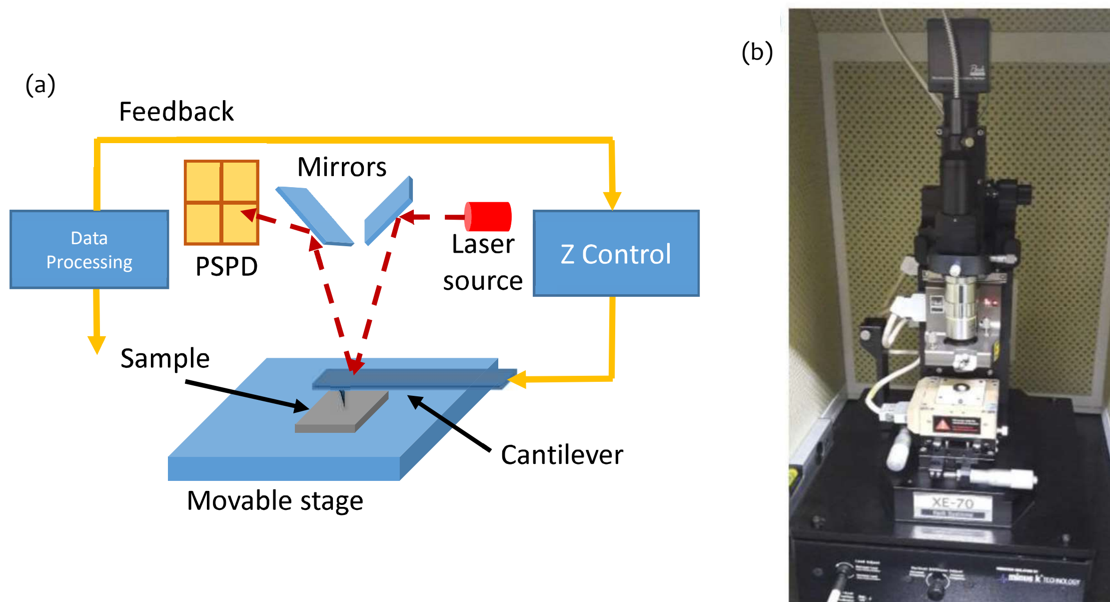


Figure 2.5: (a) Schematic representation of working of AFM (b) SPM XE-70 by Park Systems used in the characterizations in the current study

In both contact and non-contact modes, the z-displacement is measured through a laser beam which is reflected from the back surface of the cantilever. That is why the back surface of the cantilever is often coated with highly reflective gold or aluminum. Laser reflects from the back surface of the cantilever and fall on the position sensitive photo-detector (PSPD) as shown in figure 2.5(a), which measures the deflection of the laser and in turn, vertical displacement of the tip. In the present study, the atomic force microscope used was SPM XE-70, from Park Systems as shown in figure 2.5 (b).

2.6 SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy (SEM) is another widely used microscopy technology for examining micro and nanoscale features in not only semiconductor industry, but also in the field of applied physics and even biology [Egerton, 2008]. Images with the magnification of as high as 50,000x can be recorded with a resolution of 50-100 nm using SEM. As shown in figure 2.6(a), the source of the electron beam is the main component of an SEM system. Electrons emitting from the source are accelerated by an accelerating anode. Accelerating anode is followed by an electromagnetic focusing assembly which focuses the bunch of electrons into a sharp beam. For making a scanning pattern (like in a CRT screen), there are X-Y deflection coils which help the electron beam move in a predefined pattern. The scanning electron beam hits the sample which is mounted on the sample plate. Many signals are emitted due to the collision of electrons with

the sample. These signals include backscattered electrons, secondary electrons, X-ray photons, and heat. Backscattered electrons are useful in determining contrast between two different kinds of materials. The most important signal for imaging is secondary electrons. Secondary electrons help in determining the surface morphology of the sample. X-ray photons emitted from the collision help us determine the elemental composition of the material. This technique of determining the elemental composition of the material by analyzing the energy of emitted X-ray is called *Energy Dispersive X-Ray Spectroscopy* (EDX or EDS).

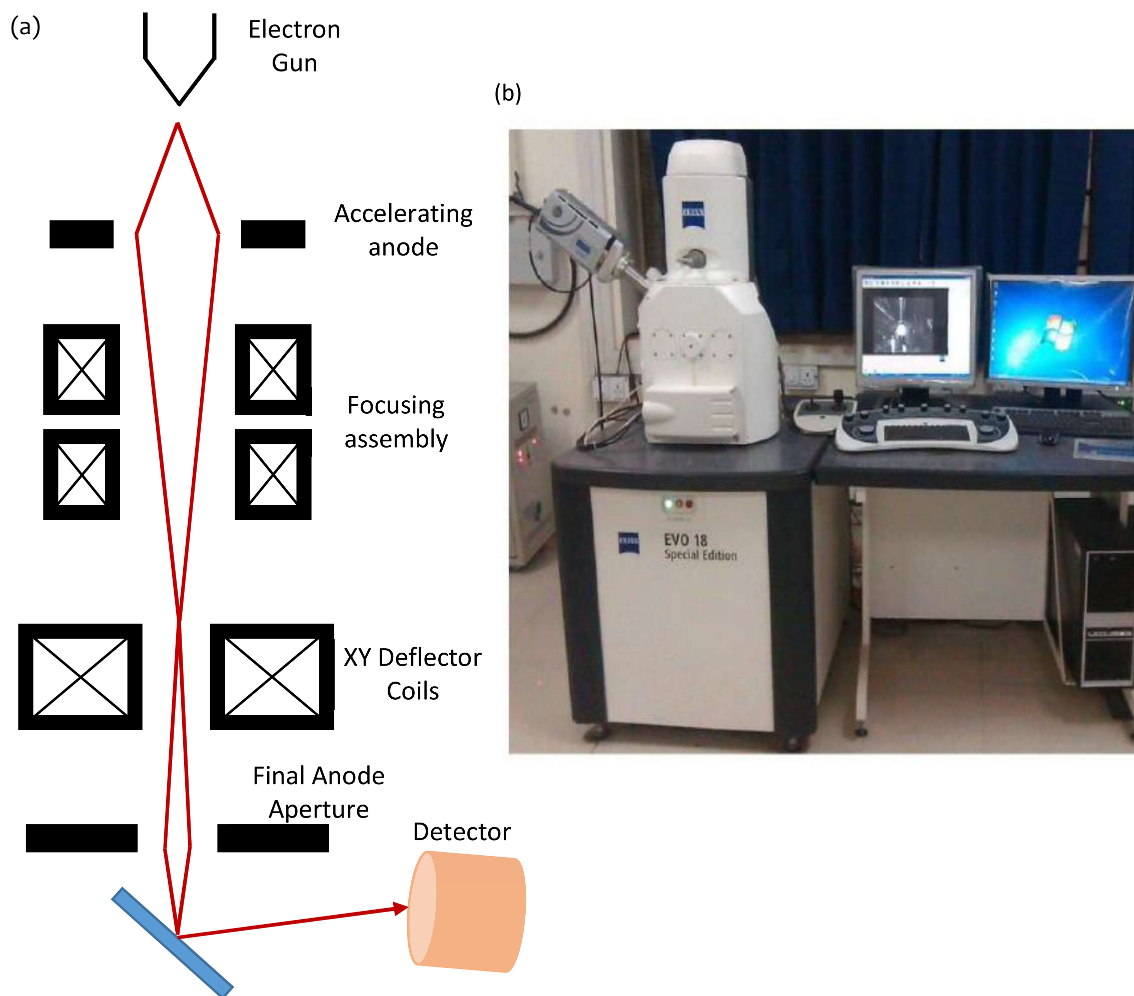


Figure 2.6: (a) Schematic and basic working principle of scanning electron microscope (b) EVO-18 special edition scanning electron microscope from Carl Zeiss used in characterization

There are two types of sources in SEM, namely-thermal emissive source and field emissive (FE) source. The SEM system used in the current study was EVO-18 special edition scanning electron microscope from Carl Zeiss as shown in figure 2.6(b).

2.7 ULTRA-VIOLET AND VISIBLE SPECTROSCOPY

Ultra-violet and visible (UV-visible) spectroscopy is a very important analysis technique for chemical analysis of the materials. This technique is used in understanding the interaction between light and matter in the UV and visible spectrum i.e. 200-800 nm. The working principle of UV visible spectroscopy is based on the absorption of the optical energy by molecules present in the sample when electrons make a transition from lower energy level to higher. In the heart of UV-visible spectroscopy, there is Beer Lambert's law, according to which the absorbance of a

solution depends on the intensity of incident radiation, absorbent's thickness, and concentration of the solution [Swinehart, 1962]. Light in a UV-visible spectrophotometer is emitted from a light source which provides light in both UV and visible ranges. A particular wavelength of light from this source is chosen with the help of monochromator. As shown in figure 2.7(a) monochromator consists of a prism which disperses the light into various different wavelengths, and a filtering slit which chooses one of the wavelengths dispersed by the prism. This monochromatic light beam is doubled using a beam splitter and is impinged onto the sample and the reference liquids filled in quartz cuvettes. The reason for using quartz instead of glass is that the glass is not entirely transparent to the UV light. The light beams passed through sample and reference are collected at the detectors, the data from which is analyzed and absorbance is calculated after the processing of the signals. The UV-visible spectrophotometer used in this study is UV1800 spectrophotometer from Shimadzu which is shown in figure 2.7(b).

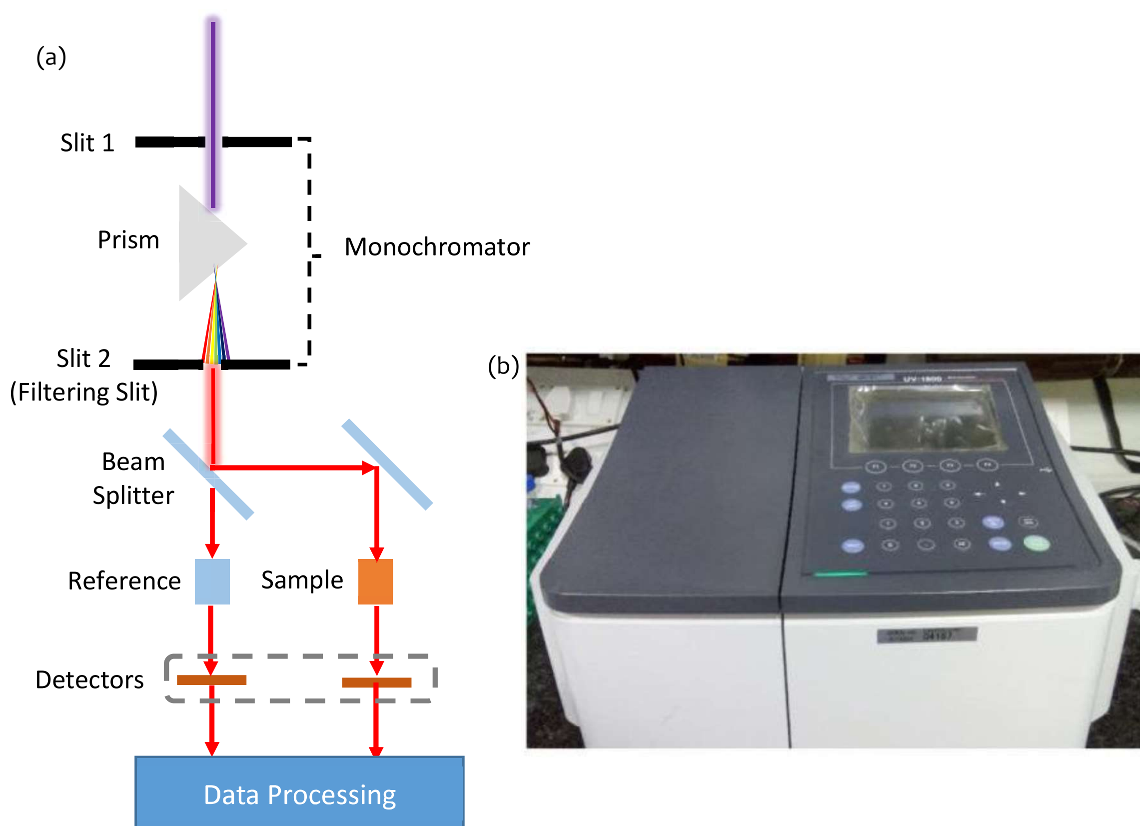


Figure 2.7: (a) Schematic diagram of basic principle of a spectroscopy system, (b) UV1800 spectrophotometer from Shimadzu, used in the characterization

2.8 ELECTRICAL CHARACTERIZATION

Electrical characterization of the memory devices fabricated was carried out using a 6430 sub femtoampere source meter by Keithley-Tektronix. As discussed in chapter 1, all three aspects of the memory device – voltage sweep, repeatability, and retention were tested using the setup. Samples were mounted in a custom made vacuum chamber which is shown in the figure, where a rough vacuum of about 10^{-2} – 10^{-3} Torr was maintained. For the measurements, customized LabView programs were developed in the lab. These programs were tailored to measure the I-V in Voltage sweep, retention time and endurance of the memory devices. The source meter was

interfaced with a computer using a KUSB 488 protocol, using a GPIB to USB converter. The contacts on the sample were made with the sharp metallic probes.

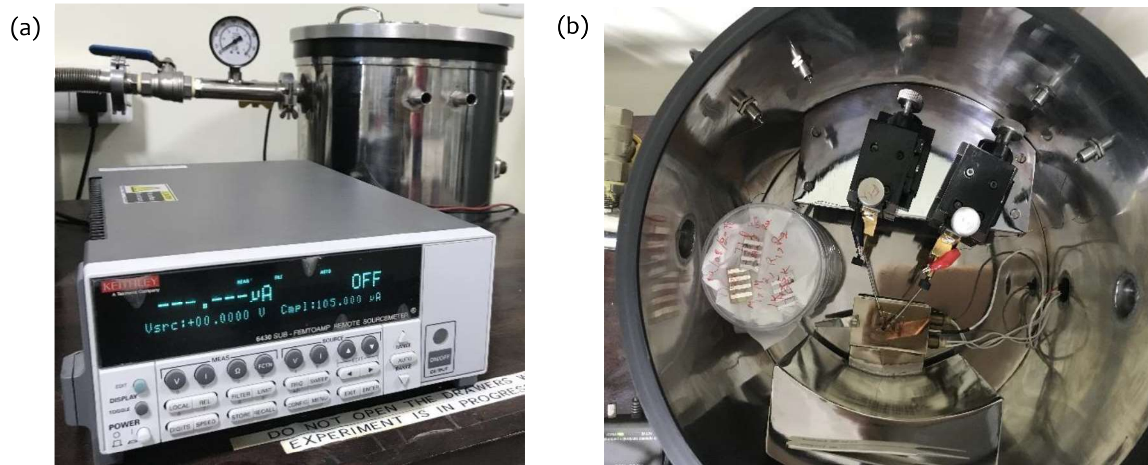


Figure 2.8: (a) Subfemtoampere 6430 source meter by Keithley-Tektronix used for electrical characterization, and the vacuum chamber in the background, (b) Top view of the vacuum chamber in which IV characterization is carried out.

2.9 CUSTOMIZED LAB VIEW PROGRAMS FOR ELECTRICAL CHARACTERIZATION

The Keithley source meter 6430 is programmable from a remote computer. It comes with a set of commands, for controlling the range, current compliance, source and sense modes, and the values of the 'source' variable. With this degree of flexibility, it is easy to develop custom programs for our specific applications regarding memory devices. All the custom programs were developed in the form of the LabView VI (LabView programs are generally termed as VIs). As discussed earlier, three basic tests were needed to be carried out on the memory devices. Voltage sweep is used to find out whether or not a particular device is showing switching, and finding ON/OFF ratio of that device. Long-run IV is used to find out the retention characteristics of the device, and repetitive read-write-erase cycles are used to find out the endurance of the memory, that how many write-read-erase-read cycles can a memory withstand without losing the voltage levels of its bistable states.

2.9.1 Voltage Sweep

The salient features of the voltage sweep program are as follows.

- The voltage sweep program used for present study is bidirectional, i.e. it sweeps the voltage from zero to a maximum value, which is entered by the user, and back to zero, and then it increases the voltage in the reverse polarity, up to a negative maximum.

- The number of iteration, i.e. the number of times the entire experiment is to be repeated can be given by the user in "Number of Iterations" control box on the front panel.

- The non-batch processing version of the program has the feature that maximum voltage in positive and negative directions can be assigned with different magnitudes. It is useful in the case of memories where write and erase voltages are different.

- In the non-batch processing version, if the maximum and minimum (positive and negative max.) voltages are reversed, then the direction of the sweep is also reversed, i.e. it starts off with the scanning in the negative direction and then goes to zero, then positive direction.

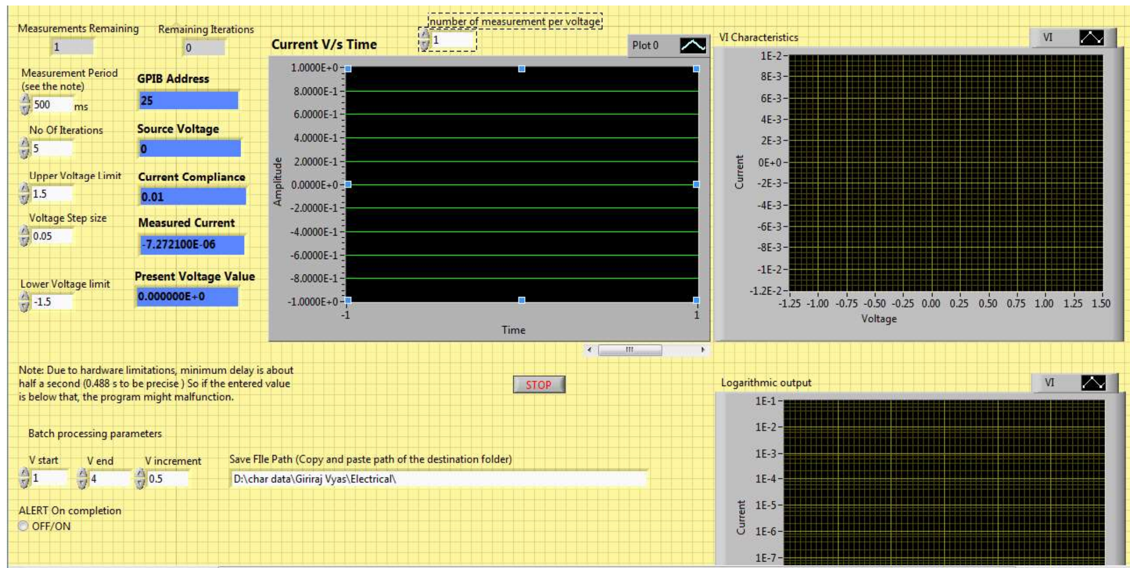


Figure 2.9: Front panel of Voltage Sweep VI with batch processing and Logarithmic output display,

- In 'batch processing' variant of the program, the user can put a range of voltages up to which the voltage sweeps are to be investigated. For example if the range of Vstart to Vend is put from 1V to 4V, with an increment of 0.5V, then the program will run a voltage sweep between 1V to -1V then repeat it for the times specified by user, then it will run a voltage sweep between 1.5V to -1.5V, and then 2V to -2V and so on till 4V to -4V.

- This program asks for the path address of the file to be saved and automatically saves results at that path after completion of each voltage sweep.

- The program also has a feature of averaging a user-specified number of consecutive current readings at the same voltage, and provide us with the average result of those points. The averaging filter is useful when the pulsed noise in the system is high which can cause an error in the measurement.

- When the dynamic scale of the output current is too large, the linear scale fails to give a correct idea of the difference of high conductance and low conductance currents and ON-OFF ratio. Hence an additional graph containing a log scale output of the absolute value of current is added to give a fair idea of the order of the current.

- An alarm goes off when the whole batch of all these sweeps has been completed which is useful to alert the end user.

- Current compliance of the source meter can be set remotely from the computer

Figure 2.9 shows the front panel of the VI of the voltage sweep whereas figure 2.10(a), 2.10(b) and 2.10(c) show the block diagram of the given program. As it is clear from the name that the block diagram provides the programming logic whereas the front panel is a user interface where the end user provides the input and can see the output.

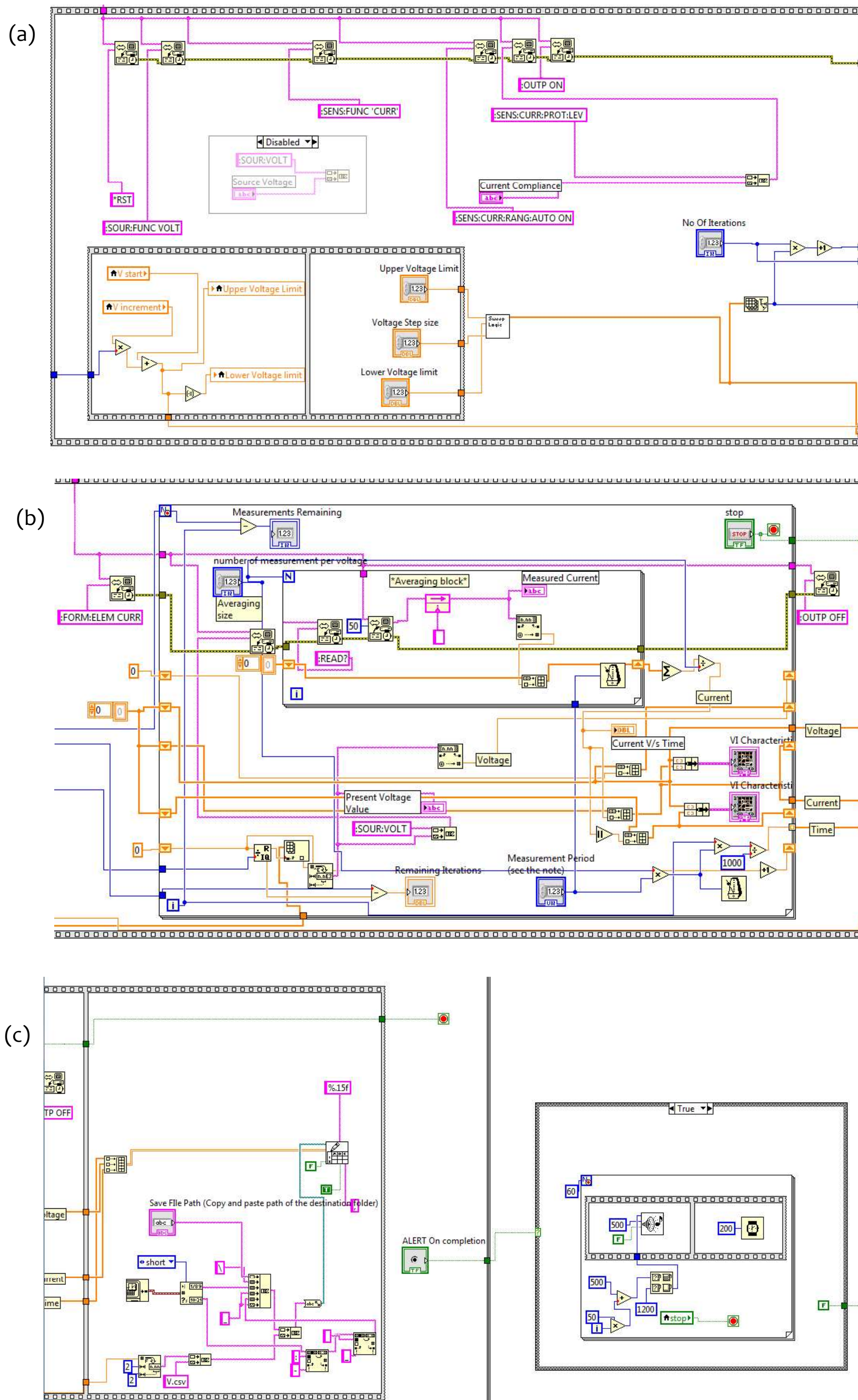


Figure 2.10: Block diagram of the Voltage sweep VI (a) Initialization of parameters, (b) Voltage sweep calculation, measurement and manipulation part, (c) saving the result and alarm notification upon completion.

2.9.2 Long-Run Program

The long-run program is designed to test the retention capability of the memory devices. Retention time is, as we have discussed earlier, the duration till the memory is able to preserve a

particular state. The long-run VI allows the user to set the 'read' and 'write' or 'erase' voltage values. The choice between 'write' or 'erase' operation is done by using a selector switch. Once selected, the user has to just run the program, and it goes on and on until the user stops it. Initially it 'writes'/'erases' the device with user-specified values for a short duration, which also can be user-defined. Then, the program just 'reads' the device for an indefinite time, until it is stopped manually. Once the user observes that a particular meta-stable state of the device is compromised, the program can be aborted. After stopping, the program asks about saving of the data, which can be saved at the desired location through a dialog box.

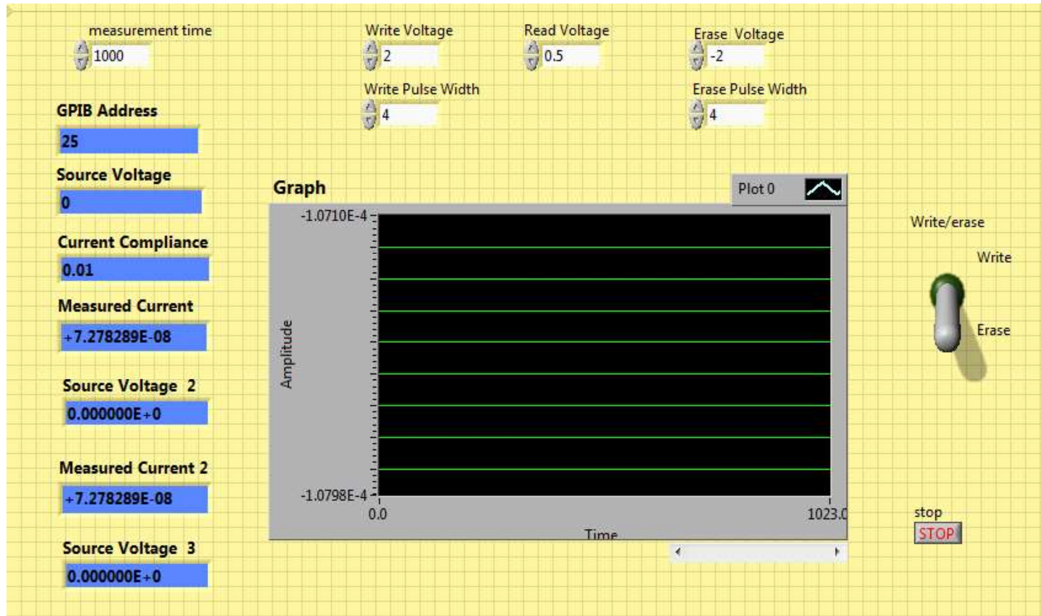
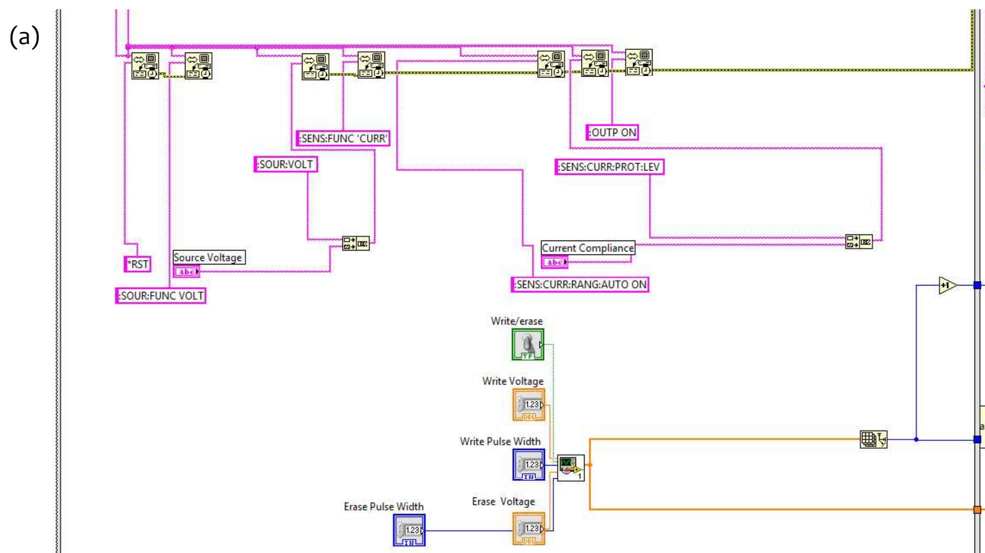


Figure 2.11: Front panel of Long-Run VI with Current v/s time display

(a)



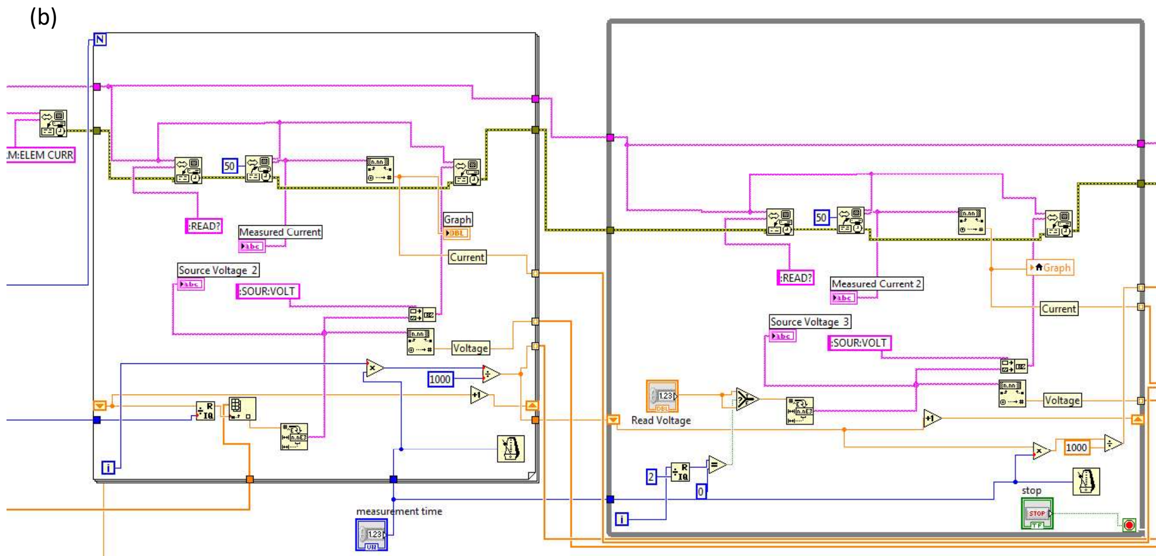


Figure 2.12: Block diagram of the Long-run VI (a) Initialization of parameters, (b) real time measurement, graph plotting and accumulation of the data.

2.9.3 Periodic Read-Write-Erase Program

This program is used to test the endurance of the device. The user enters read, write and erase voltages and the time duration for which these voltages are to be applied. Upon running the program, a sequence of Erase-Read-Write-Read pulses are applied to the device and current values are plotted with respect to the time. This repetitive cycle runs as many times as the user has specified in the given field. Endurance is a very crucial data for a memory device, as it signifies the durability and reliability of the device fabricated.

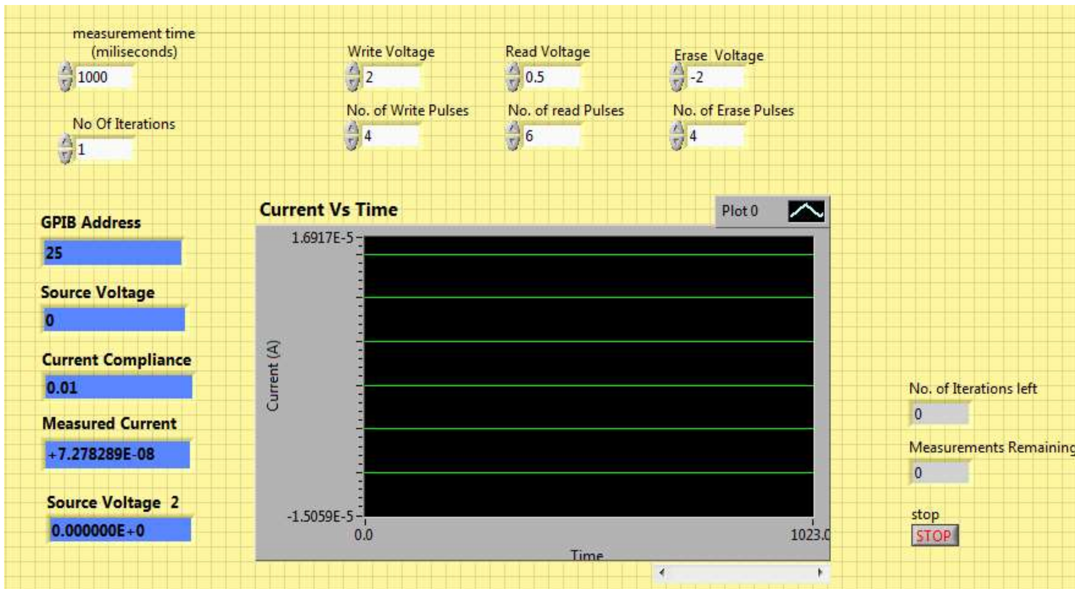


Figure 2.13: Front panel of the periodic read-write-erase VI.

(a)

(b)

Figure 2.14: Block diagram of the periodic Read-Write-Erase VI (a) Initialization of parameters, (b) real time measurement and graph plotting, and the accumulation of the data.

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