Chapter 2

In this chapter, different experimental techniques that are used in this thesis work have been discussed. These experimental techniques include different materials synthesis, material characterization, and thin-film device fabrication-characterizations. In the material synthesis section, two different types of materials have been discussed; one of them is ion-conducting oxide dielectric, and the other one is metal oxide semiconductor. Material characterization parts include different bulk material and thin film characterization. Device fabrication includes MIS and TFT fabrication, whereas electrical characterization includes, current vs. voltage (I-V), capacitance vs. frequency (C-f) measurement.

2.1 Material Synthesis

As mentioned earlier, two different classes of metal-oxides materials are synthesized in this thesis with a low-cost solution processing technique (sol-gel method) for the fabrication of metal oxide thin-film transistor (TFT). These two metal oxides materials are i) ion-conducting oxide insulator and ii) metal oxide semiconductor. Out of these two materials, an oxide insulator acts as a gate dielectric of an oxide semiconductor works as an active channel of a TFT. This sol-gel method is allowing the substance to react uniformly at a molecular level and capable of creating a single polycrystalline thin-film compound. Mostly metal salts which are easily dissolved in alcohol have been used as the precursor materials for the synthesis of dielectric or semiconductor layer.

2.1.1 Dielectric material: Li_2ZnO_2

The Li_2ZnO_2 dielectric thin film was synthesized by the sol-gel method and used as a gate insulator for metal oxide thin-film transistors. For the synthesis of Li_2ZnO_2 dielectric

synthesis, zinc acetate dihydrate (Zn $(CH_3CO_2)_2 \cdot 2H_2O$) and lithium acetate (CH_3COOLi) have been used as a precursor material. Initially, a 300 mM solution of zinc acetate dihydrate was prepared by using 2-methoxyethanol (2-ME) solvent. The mixture was stirred for 1hour to form a fully transparent solution. A solution of lithium acetate was also prepared in a similar way with the same solvent and concentration. Then, both the solutions were mixed in the desired amount, i.e. (2:1) ratio, and stirred for 10 minutes more at room temperature to prepare a clear homogenous solution which was used for Li_2ZnO_2 dielectric thin film deposition. A separate portion of 300 mM lithium acetate solution was kept to use as a precursor for Li_2O gate dielectric. Finally, both types of solutions were filtered through a 'syringe filter' (0.45mm) to remove the unwanted impurity particle. A portion of this precursor solution was dried to obtain a mixture of zinc acetate dihydrate and lithium acetate that was used to prepare a powder sample for differential thermal analysis (DTA) and X-ray powder diffraction (XRD) analysis.

2.1.2 Dielectric material: $LiInO_2$ and $LiGaO_2$

The $LiInO_2$ and $LiGaO_2$ precursor solutions, which are used as an ionic gate dielectric for metal oxide TFT was synthesized by a low-cost sol-gel method. A separate 300 mM precursor solution of lithium acetate (CH_3COOLi), indium chloride ($InCl_3$), and gallium nitrate ($Ga(NO_3)_3$) were dissolved in 2-methoxyethanol (2-ME) and stirred at room temperature for one hour and 24 hours respectively. The indium chloride and gallium nitrate precursor solutions were aged for one day at room temperature. Both solutions were mixed with lithium chloride solution in the desired ratio and again stirred for one hour at room temperature. Finally, a transparent precursor solution formed, which was used to deposit a gate dielectric for metal oxide TFT. A portion of the precursor solution was separated and

was kept on a hot plate at 100 ^{o}C for 12 hours to prepare a powder gel by removing the solvent. That powder sample was used for material characterization, including X-ray diffraction (XRD) and thermal analysis.

2.1.3 Dielectric material: Li_5AlO_4

Similar to Li_2ZnO_2, crystalline, Li_5AlO_4 dielectric thin film was synthesized by the sol-gel technique and successfully used as a gate dielectric for the Graphene field-effect transistor (GFET). Lithium acetate (CH_3COOLi) and Aluminum tri-secondary butoxide [$Al(OC_4H_9)_3$] used as precursor materials for the synthesis process. At first, a known concentration of alumina sol was prepared by the Yoldas process, and lithium acetate solution was also prepared with the same concentration by using 2-methoxyethanol (2-ME) solvent. Afterward, both solutions were mixed with preferred amounts to preserve Li and Al content with a 5:1 ratio in the final ceramic product. The solution was then stirred at room temperature for 30 minutes to prepare a clear homogeneous solution. A portion of the precursor solution was separated and was kept on a hot plate at 120 ^{o}C for 6 hours to prepare a powder gel by removing the solvent. That powder sample was used for material characterization, including X-ray diffraction (XRD) and thermal analysis.

2.2 Semiconductor material: SnO_2

Sol-gel derived tin dioxide (SnO_2) has been used as a semiconductor for most of the metal oxide TFT reported in this thesis. To synthesis semiconductor by solution-processed technique, a 300 mM precursor solution of SnO_2 was prepared using $SnCl_2$ as a precursor material. A measured amount of tin (II) chloride was dissolved in 2-methoxyethanol (2-ME) and stirred for one hour at room temperature and used as a channel layer of TFT.

2.3 Device fabrication

The whole device fabrication flow of process with cleaning steps is shown in **figure 2.1**

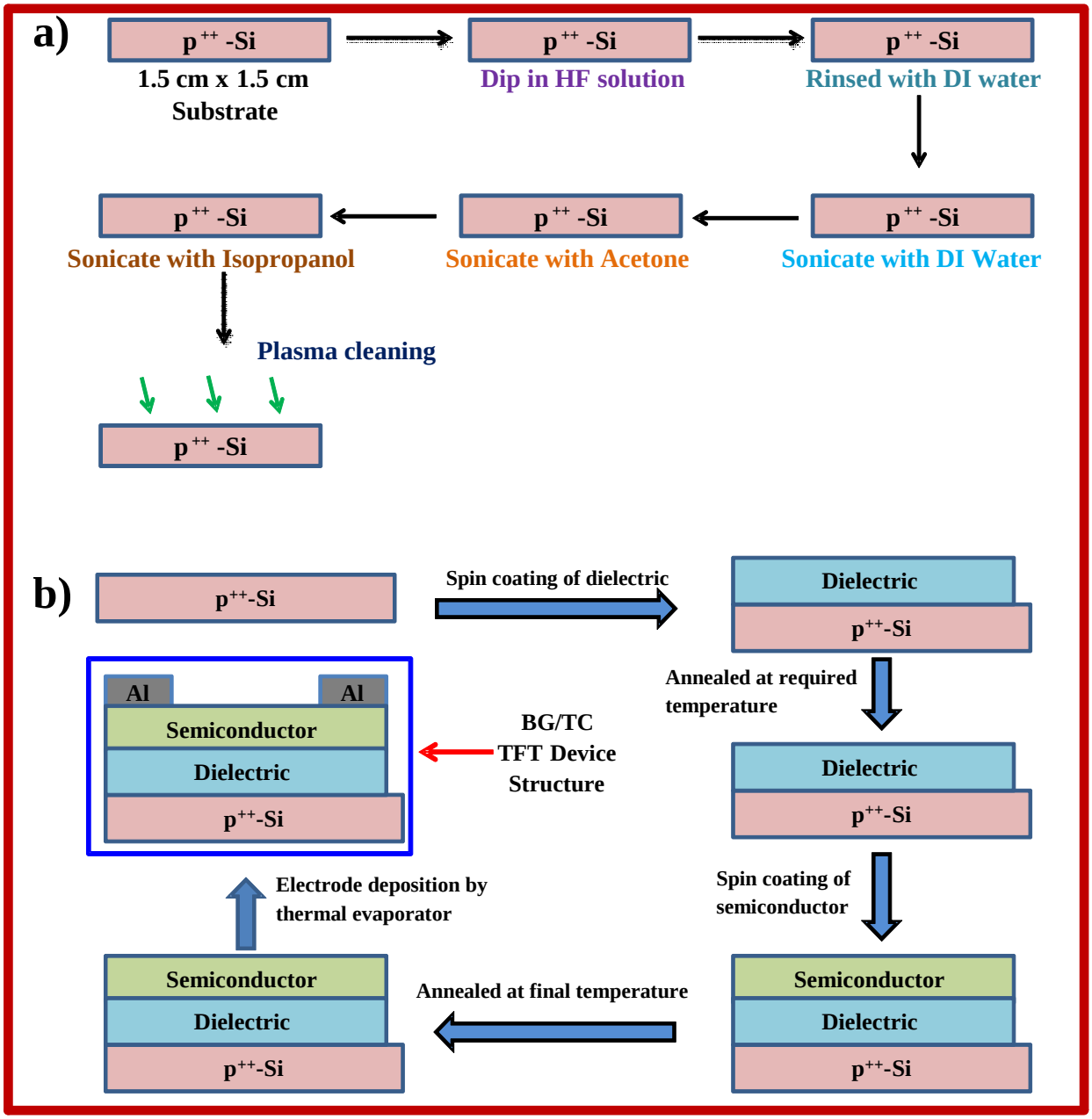

Figure 2.1: a) *Flow chart of the cleaning process and* ***b)*** *flow chart of the device fabrication.*

2.3.1 SnO_2 TFT fabrication by using Li_2ZnO_2 dielectric

In all of our experiments, bottom-gate top-contact thin-film transistors were fabricated on heavily doped (p^+-Si) silicon substrate. To fabricate such kinds of devices, in the beginning, p^+-Si wafers of size 15 mm x 15 mm were cleaned by soap solution followed by cleaning in water, acetone, and iso-propanol, respectively for 30 minutes each in an ultra-sonication bath. After wet cleaning, the wafers were dried by passing dry air. Finally, all the substrates were cleaned by oxygen-plasma to make them hydrophilic, which is a very crucial step in sol-gel derived thin film fabrication that allows high uniformity of the film and capable of depositing film without pin-hole with minimum trap states. After the cleaning process, the precursor sol of Li_2ZnO_2 was spin-coated on silicon substrates at 4000 rpm for 60s under ambient atmospheric conditions. Spin-coated samples were immediately kept on a pre-heated hot plate at 80 ^oC for two minutes to remove the solvent and make it dry. After drying, the samples were annealed at the temperature of 350 ^oC in a furnace for 30 minutes. Then this process was repeated two more times, and finally, the thin film was annealed at 500 ^oC for 30 minutes under the ambient atmospheric condition to obtain the polycrystalline phase of Li_2ZnO_2. For semiconductor deposition, a 300 mM solution of SnO_2 was coated on top of Li_2ZnO_2 coated p^+-Si substrate at 3000 rpm followed by a drying process on a pre-heated hot plate at 120 ^oC for 5 minutes. These dried samples were immediately transferred to a pre-heated high-temperature furnace at 500 ^oC to anneal the sample for 30 minutes that forms a polycrystalline SnO_2 thin film on Li_2ZnO_2 dielectric layer. The same procedure was followed for Li_2O dielectric based SnO_2 TFT fabrication. Finally, the aluminum source and drain electrode were deposited by thermal evaporator on top of the SnO_2 layer under a pressure of 6.0×10^{-6} Pa with a shadow mask to complete the TFT fabrication.

2.3.2 SnO_2 TFT fabrication by using $LiInO_2$ or $LiGaO_2$ gate dielectric

We have fabricated bottom gate top electrode TFT with heavily doped p-type Si (p^+-Si) substrates of dimension 15 mm x 15 mm. At first, all these substrates were wet cleaned through the routine cleaning processed, as mention previously. Then the substrates were dried by passing dry air followed by the oxygen plasma cleaning process for 5 minutes to remove unwanted organic residue (hydrocarbons) from the Si substrate and make the substrate hydrophilic. Before spin coating, all precursor solution filtered through syringe filter MVDF 0.45µm due to which film quality improved. Afterward, the solution of dielectric precursor $LiInO_2$ was spin-coated at 4000 rpm for 50 seconds on the top of Si-substrates under ambient atmospheric conditions. To remove the precursor solvent, the spin-coated film was kept on a hot plate at 80 ^oC for two minutes, and then, the sample was transferred to a muffle furnace to anneal it at 350 ^oC for half an hour. This process was repeated two more times. Finally, the dielectric thin film coated on Si substrate annealed in a furnace at 500 ^oC for one hour to obtain the polycrystalline phase of $LiInO_2$ under ambient atmospheric condition. A tin oxide (SnO_2) thin film was used as a metal oxide semiconductor that was deposited on the ionic gate dielectric by another sol-gel process. For this, a 300 mM precursor solution of SnO_2 was spin-coated onto dielectric $LiInO_2$ or $LiGaO_2$ film and kept on a pre-heated hot plate at 120 ^oC for 2 minutes and then annealed in a furnace at 500 ^oC for half an hour to achieve polycrystalline thin film of SnO_2 on the dielectric surface. The aluminum metal was used as a source and drain electrode for TFT, which was deposited by a thermal evaporator on the top of the semiconductor with a shadow mask under a high vacuum with a width to length ratio of 118 (W/L= 23.6 mm/0.2 mm).

For the measurement of leakage current and capacitance of the dielectric, a device of p^+-Si/dielectric/Al geometry was fabricated under the same condition. Likewise, for atomic force microscope (AFM) and X-ray diffraction studies, a dielectric film was deposited on p^+-Si in the same condition.

2.3.3 Graphene field-effect transistor (GFET) fabrication by using Li_5AlO_4 gate dielectric

All bottom-gate top-contact GFETs were fabricated on heavily doped (p^+-Si) silicon substrate. Before the fabrication of these types of devices, the p^+-Si-wafers (15 mm x 15 mm) were cleaned by the standard cleaning process. After wafer cleaning, precursor sol of ionic gate dielectric of Li_5AlO_4 was spin-coated on p^+-Si substrates at 4500 rpm for the 50s under the ambient atmospheric condition and subsequently kept on a pre-heated hot plate at 70 ^oC for two minutes to remove the solvent and make the film dry. After drying, the samples were annealed in the furnace for 30 minutes at the temperature of 350 ^oC. The same process was repeated two more times, and finally, all thin film samples were annealed at 500 ^oC for 30 minutes under the ambient atmospheric condition to obtain polycrystalline α-phase of Li_5AlO_4. Graphene layer, which works as an active channel of GFETs, was deposited on the top of the Li_5AlO_4 layer by following the standard polymer assisted graphene transfer method. In addition, graphene films were also transferred on a 300 nm oxide coated doped Si wafer (p^+-Si/SiO_2). Finally, a silver electrode (Ag) with a molybdenum oxide (MoO_x) interface was deposited on both types of the substrate by thermal evaporation process that has been used as a source and drain electrodes of GFET. These source and drain electrodes were fabricated by the shadow-mask process under a pressure of 7.0 x 10^{-6} mBar. Six different large channel length GFETs were fabricated with fixed channel width (W) of 9 mm but with

variable channel lengths (L) ranging from 0.2 mm to 5.7 mm. Accordingly, W/L ration of these GFETs were varied from 118 to 1.57.

2.4 Material characterization

2.4.1 Thermal analysis

Thermogravimetry (TG), the technique for monitoring the weight loss of a sample against time or temperature (e.g., decomposition, dehydration, and oxidation), is performed with a thermogravimetric analyzer (TGA). Mass is lost if there is a volatile fraction in the substance. This characterization is very efficient in checking the thermal stability of the material in different atmospheres. Therefore, a Mettler Toledo thermogravimetric analyzer (TGA) was used to analyze the mass loss rate of the precursor materials that have been used for the deposition of ion-conducting oxide dielectric. Nitrogen has been used to maintain an inert atmosphere during the whole measurement. Approximately 3 mg of sample was placed on the crucible and scanned in the temperature range of 40 to 800 ^{o}C at a rate of 20^{o}/ min. The temperature corresponding to 5 % weight loss was taken as degradation temperature. Also, the same instrument functioned as Differential Thermal Analysis (DTA) has been used to determine glass transitions, melting, sublimation, and crystallization temperature of the precursor materials. This differential temperature has been plotted against temperature to identify the exothermic or endothermic heat flow between source and sample.

2.4.2 X-ray diffraction

X-ray powder diffraction (XRD) is a fast investigative method that used primarily to identify the crystalline phase of material and the lattice parameters of a unit cell. To check the crystal structure of thin film and the synthesized powder, Rigaku wide-angle X-ray diffractometer instrument has been used. The Cu Kα having a wavelength of 0.15406 nm, is used as a

source with a generator function having a current 200 mA at an operating voltage of 45 kV. The samples are placed on the sample holder, and the scans are conducted from 2^{o} to 80^{o} diffraction angle, with a scan rate of 3^{o}/ min.

2.4.3 UV-visible spectroscopy

A spectrophotometer is a device used as a function of the wavelength of the electromagnetic spectrum to measure the absorption or transmittance of a sample. This instrument has been used to identify the visibility of sol-gel-coated dielectric thin film. UV-Vis spectroscopic measurement of the dielectric's thin films was performed by using the JASCO V-650 spectrophotometer within a frequency range of 200-800 nm wavelength.

2.4.4 Atomic force microscope

Since the dielectric/semiconductor interface plays an essential role in the performance of the thin-film transistors, the characterization of surface morphology of dielectric thin film is very crucial. As it is known that the rough interface (dielectric/semiconductor) always acts as transport barriers and hinders the transportation of charge carriers in semiconductors, it is essential to fabricate high-quality dielectric thin film with very low roughness. A charge carrier requires higher energy to cross the interface of the rougher surface; hence the overall mobility of TFT gets suppressed. The surface roughness measurement of the dielectric thin film was therefore explored with the strong nanometer resolution atomic force microscopy instrument (AFM). An AFM operates in a distinct mode depending on the distance between the cantilever tip and the surface of the sample. The NT-MDT multimode AFM (Russia) was used to scan the bulk surface morphology of the samples, controlled by a Solver scanning microscope controller. The semi-contact mode of AFM is used to calculate the root mean square roughness of the sol-gel coated dielectric thin film. A 100 μm long, single beam

cantilever was used for the semi-contact mode with a tip mounted with a resonant frequency range between 240 and 255 kHz and the corresponding spring constant of 11.5 Nm^{-1}.

2.4.5 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is the quantitative spectroscopic surface-sensitive technique that measures elementary composition; the analytical formulation; the chemistry state; and the electronic condition of the substance. In my thesis work, I have used XPS to check element composition, chemical state, and electronic state to our ion-conducting oxide dielectric materials.

2.4.6 Leakage current density measurement

Measurement of the leakage current density is one important characterization of the dielectric thin film prior to TFT production. Since the dielectric material electrically isolates the gate electrode from source and drain electrodes, ideally, no current should be allowed to flow through the dielectric thin film. Though, very small current passes due to the existence of few traces or pin-hole in the thin film. Therefore, this leakage current measurement tells us the quality of the dielectric thin film and predict the order of the leakage current in the fabricated TFT. Using an Agilent B1500A semiconductor parameter analyzer, current-voltage density features of MIM devices (p^+-Si / dielectric / Al) were done in an open atmosphere. The layout of the device structure is shown in **figure 2.2**.

2.4.7 Capacitance-frequency (C-*f*) measurements

Another important parameter for checking the feasibility of the gate dielectric is capacitance-frequency (C-*f*) measurement. The same metal-insulator-metal (MIM) structure has been used for this measurement. The effective area of the capacitor is the area of the mask used in

the metallization of the top electrode. The dielectric constant of the gate insulator can be calculated by measuring the capacitance value. This measurement has been done using an LCR meter (Keysight LCR meter E4990A) with a device structure of p^+-Si/dielectric/Al at a frequency range between 20 Hz to 10 MHz. The schematic device structure of the capacitance-frequency measurement structure is shown in **figure 2.2**.

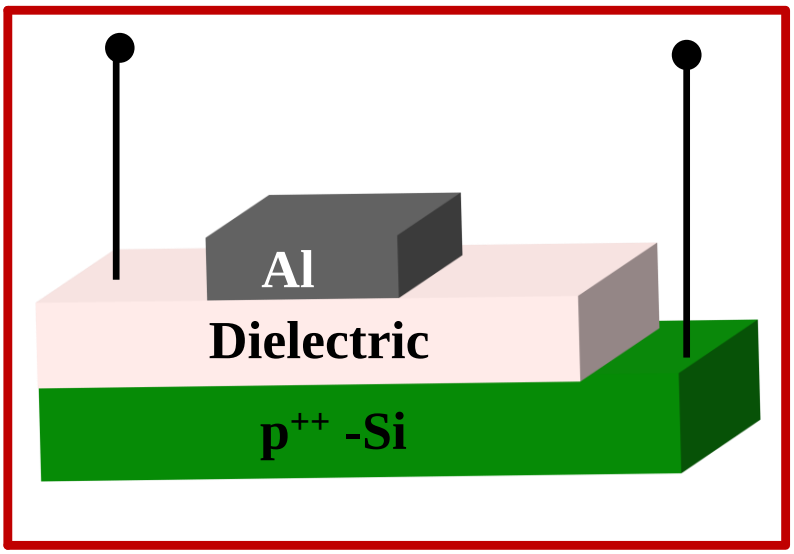

Figure 2.2: *Arrangement of the MIM device structure for C-f and I-V measurements.*

2.4.8 Thin film transistor characterizations

Since TFT is a three-terminal device, electrical characterization of it required two sets of measurements. The layout of the TFT device is shown in **figure 2.3**. If drain current (I_D) is measured with respect to drain voltage (V_D) under constant gate voltage (V_G), the characteristics are called output characteristics (V_D vs. I_D). On the other hand, when I_D is measured with the variation of V_G under constant V_D, the characteristics are called transfer characteristics (I_D vs. V_G). The output characteristics are the primary electrical characterization to check the quality of the TFT operation. This characteristic provides the linear and saturation region of the device. However, the transfer characteristics are more

important because it gives the all-important device parameter of TFT, including mobility, on/off ratio, the threshold voltage (V_{th}), etc. All these TFT characterizations were performed in ambient atmospheric conditions. Electrical measurements were carried out using an Agilent B1500A semiconductor parameter analyzer. The electrical contact of TFT was made by using probe micromanipulator. The electron mobility was extracted from the transfer characteristics by using the gradual channel approximation.

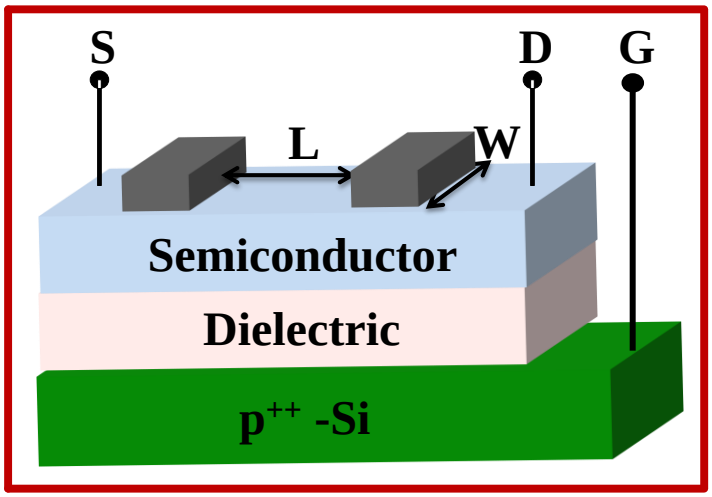

Figure 2.3: *Layout of the BG-TC device structure for TFT characterization.*