Chapter 2

Experimental Section: Material Synthesis & Characterization, Device Fabrication and characterization.

Chapter-2

To achieve the key objectives of our thesis we have fabricated different metal oxide thin-film transistors an overview of which has already been given in the previous chapter. For the fabrication of these thin-film transistors, different metal oxide dielectrics and metal oxide semiconductors have been synthesized. Besides, this TFT fabrication thin-film device with an MIS structure was fabricated to characterize the dielectric thin film. In the characterization part of our work, we have discussed about the materials (Bulk and Thin-film) characterization and device characterization. In addition, different experimental methodologies that are employed in this thesis work have been discussed in this chapter as well.

2.1 Material preparation-

To fabricate these TFTs, two different classes of metal oxide materials are synthesized by using a low-cost solution processing approach. One is an oxide insulator, which serves as the TFT's gate dielectric, and the other is a metal oxide semiconductor, which serves as the active channel of the transistor. This solution-processing method, also known as the sol-gel method, allows the material to react uniformly throughout the thin film at the molecular level, resulting in a single compound polycrystalline thin film. Different metal salts were used for these material syntheses that are dissolved in various alcoholic solvents. These precursor solutions were used as dielectrics or semiconductors thin film deposition of TFT.

2.1.1 Preparation of $Pb_{0.8}Ba_{0.2}ZrO_3$ Dielectric-

As mentioned earlier, $Pb_{0.8}Ba_{0.2}ZrO_3$ (PBZ) dielectric thin film was successfully produced using the sol-gel method and employed as a gate dielectric for metal oxide TFTs. For the preparation of the precursor solution of this PBZ dielectric thin film, 2-methoxy ethanol has been used as a solvent and lead acetate $Pb(C_2H_3O_2)_2$, barium nitrate $Ba(NO_3)_2$, and zirconyl nitrate $Zr(NO_3)_4$ were used as the source of Pb, Ba, and Zr respectively. Separately, 300 mM concentrations of lead acetate, barium nitrate, and zirconyl nitrate were dissolved in a 2-methoxy ethanol solvent to make a precursor solution. Then, to maintain the Pb, Ba, and Zr ratios, these solutions were combined in the appropriate ratio. To make a clear homogenous solution, the combined solutions were agitated for 2 hours at room temperature. The solution was filtered using a syringe filter (0.45 μm) to remove the undesirable larger particles before being employed as a gate dielectric for TFTs. To make a powder gel by eliminating the solvent, a portion of the precursor solution was separated and maintained on a heated plate at 90^oC for 12 hours. That powder sample was used to grow the PBZ powder sample which has been used for several material characterizations, including thermal gravimetric analysis (TGA), differential thermal analysis (DTA), and X-ray diffraction (XRD).

2.1.2 Preparation of $SrTiO_3$ Dielectric-

Like PBZ dielectric, a low-cost sol-gel process was employed to make the $SrTiO_3$ which was used to fabricate the perovskite thin-film transistor. For this, 300 mM concentration of strontium nitrate $Sr(NO_3)_2$ and titanium butoxide $Ti(C_4H_9O)_4$ precursor salts were dissolved in 2-methoxy ethanol (2-ME) and stirred at room temperature for one hour. At room temperature, these precursor solutions were aged for one day. Both solutions were combined in the required ratio (1:1) and stirred for one hour at room

temperature. Finally, a transparent precursor solution was obtained, which was utilized to deposit as a gate dielectric. To make a $SrTiO_3$ powder sample, the solvent of the precursor solution was removed by keeping it on a hot plate (90^oC) for 12 hours followed by an annealing process. Material characterization, including X-ray diffraction (XRD) and thermal analysis, were performed on that powder $SrTiO_3$ sample.

2.1.3 Preparation of $BaTiO_3$ Dielectric-

Like PBZ and STO, $BaTiO_3$ dielectric thin films are also made by the sol-gel process and employed as gate insulators for perovskite oxide thin-film transistors, as previously described. Barium nitrate and titanium butoxide were employed as starting materials for the $BaTiO_3$ dielectric synthesis. Using 2-methoxy ethanol as a solvent, a 300 mM solution of Barium nitrate was first produced. To make a perfectly clear solution, a few drops of water were added and the mixture was agitated for 2 hours. In the same method, a solution of titanium butoxide with the same concentration was made with the same solvent. Then, at a 1:1 ratio; both solutions were combined and stirred for another 1 hour at room temperature to produce a transparent homogeneous solution that was utilized for $BaTiO_3$ dielectric thin film deposition. A fraction of the precursor solution was dried, and powder samples were prepared for thermal gravimetric analysis (TGA) and X-ray powder diffraction (XRD). To eliminate the undesirable impurity particle, the solution was filtered using a syringe filter' (0.45 mm).

2.1.4 Preparation of Li_2SnO_3 Dielectric-

Like all other dielectric materials, a solution-processed approach was used to make crystalline Li_2SnO_3 thin film, which is used as a gate dielectric in low voltage TFTs. For the amalgamation of Li_2SnO_3, lithium acetate dihydrate ($C_2H_3LiO_2$. $2H_2O$) and tin chloride ($SnCl_2$) were used as precursor materials. Separate solutions of $SnCl_2$ and

$C_2H_3LiO_2$ of concentration 300 mM were prepared in a 2-methoxy ethanol solvent at the beginning of this synthesis. For homogenous mixing and transparency, individual solutions were agitated for 1 hour. Then $SnCl_2$ and $C_2H_3LiO_2$ solutions were blended with 1:2 ratios and stirred for 15 minutes at room temperature. For thermal gravimetric analysis (TGA) and XRD study, fractions of this initially produced solution were dried and collected for powder Li_2SnO_3 sample preparation.

2.1.5 Preparation of bilayer TiO_2/Li_2SnO_3 bilayer Dielectric-

To enhance the transistor performance, a bilayer dielectric of TiO_2/Li_2SnO_3 was employed between a gate electrode and semiconductor layer. The SnO_2 thin film has been used as a semiconductor channel to fabricate the metal oxide TFT. A 300 mM solution of lithium acetate dihydrate ($C_2H_3LiO_2$. $2H_2O$) and tin chloride ($SnCl_2$) were prepared by stirring it for 1 hour followed by mixing those two solutions in the required molar ratio(1:1). A 300 mM precursor solution of TiO_2 was prepared by dissolving titanium butoxide in 2-methoxyethaol and stirring for 3 hours at 60 ^oC for TiO_2 deposition.

2.2 Preparation of IZO Semiconductor-

Indium zinc oxide (IZO) was synthesized using the sol-gel method and was employed as the channel semiconductor in one of the TFTs presented in this thesis. A separate 300 mM IZO precursor solution was prepared for the metal oxide semiconductor thin film deposition. As starting ingredients, stoichiometric amounts of reagent grade indium chloride ($InCl_3$, 99 %) and zinc acetate ($(CH_3COO)_2Zn$, 99 %) were used. A certain quantity of zinc acetate was dissolved in 2-methoxy ethanol (2-ME) and agitated at room temperature for 30 minutes. In this solution, around 2% Diethanolamine (99% by volume) was utilized as a stabilizer. Similarly, $InCl_3$ was dissolved in 2-ME in a separate solution. After that, both solutions were added in a 7:3 (In: Zn) molar ratio and

rapidly agitated for 2 hours before being utilized to deposit the semiconductor layer in TFT. Before thin film deposition, these precursor solutions were filtered using a syringe filter (MVDF, 0.45μm) to eliminate any undesirable particles.

2.2.1 Preparation of SnO_2 Semiconductor-

For the majority of the metal oxide, TFTs reported in this thesis have been fabricated by using sol-gel-derived tin dioxide (SnO_2) as a semiconductor. A 300 mM precursor solution of SnO_2 was prepared by dissolving $SnCl_2$ salt in 2-methoxy ethanol (2-ME) which was stirred at room temperature for one hour before being employed as a TFT channel layer.

2.3 Fabrication of TFT Device-

Bottom-gate top-contact thin-film transistors were fabricated on a highly doped silicon (p^{++}-Si) substrate in all of our work. To make such devices, p^{++}-Si wafers (15 mm x15 mm) were first washed in a soap solution, water, acetone, and iso-propanol for 30 minutes respectively inside an ultra-sonication bath.[119, 153, 154] After wait clearing, the wafers were dried with dry air. Finally, all of the substrates were cleaned with oxygen plasma to make them hydrophilic, which is an important step before sol-gel thin film deposition, as it allows for excellent homogeneity of the thin film. After dry cleaning, a precursor sol of dielectric was spin-coated on silicon substrates for 40 seconds at 4000 rpm in ambient air. To remove the solvent from the film, the spin-coated samples were placed on a pre-heated hot plate at 90 ^oC for two minutes. After drying, the samples were annealed in a furnace for appropriate time and temperature. With the same technique, we coat the semiconductor on top of the dielectric layer and finally, the metal electrodes were deposited by a thermal evaporator which will work as a source and drain. The following flow diagram shows the different steps used for thin-film transistor fabrication.

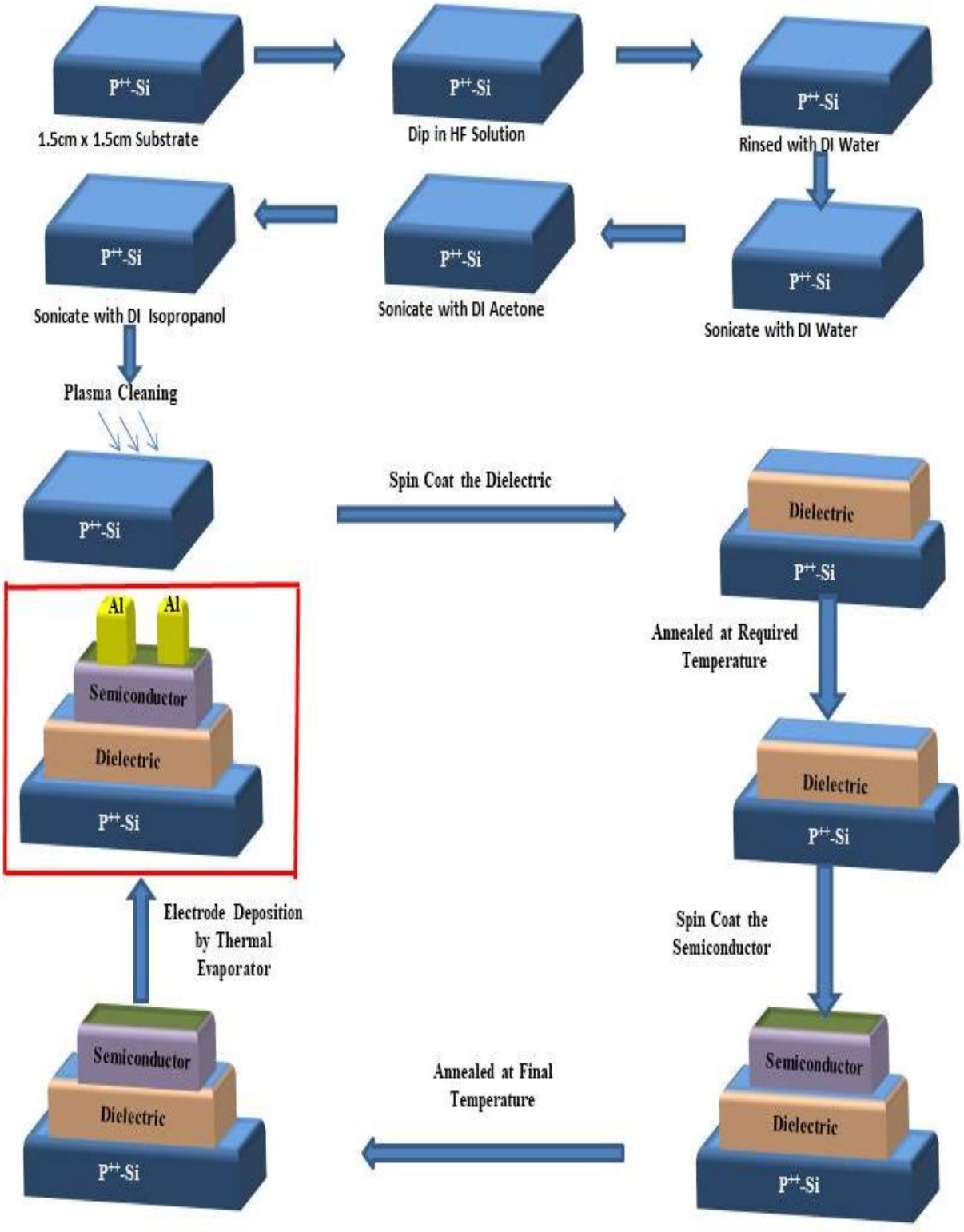

Figure 2.1: Flow chart of thin-film transistor fabrication.

2.3.1 Fabrication of IZO TFTs with $Pb_{0.8}Ba_{0.2}ZrO_3$ as a dielectric-

All TFTs were built on a 15 mm x 15 mm heavily doped silicon (p^{++}-Si) substrate. As mentioned in an earlier section, cleaning the substrate is the first stage of the TFT fabrication process. After cleaning, the precursor sol of PBZ was spin-coated on top of p^{++} -Si substrates at 4000 rpm for 60 seconds followed by a drying process on a prepared hot plate at 80°C for 2 minutes. After that, samples were annealed for 30 minutes at 350°C. This process was repeated one more time to get an appropriate thickness of the dielectric thin film. Finally, the dielectric film was annealed at 550°C/30 minute and then 830°C/30 minutes under ambient conditions. These annealing stages result from a polycrystalline PBZ thin film. For metal-oxide-semiconductor deposition, a 300 mM IZO precursor solution was spin-coated with a speed of 4000 rpm for 60 seconds on top of the PBZ dielectric layer, then annealed at 500°C for 30 minutes in ambient air. To finish the TFT fabrication, aluminum electrodes were deposited on the IZO film using a thermal evaporator under a pressure of 10^6 Pa using a shadow mask to deposit source and drain electrodes with a width-to-length ratio (W/L) of 118.

2.3.2 Fabrication of SnO_2 TFTs with $SrTiO_3$ as a dielectric-

A bottom gate top contact thin film transistor on heavily doped p^{++}-Si was fabricated. To eliminate the undesirable native oxide that had developed over the surface of the substrate, p^{++}-Si wafers (15 mm x 15 mm) were cleaned by the same process and exposed to plasma in plasma cleaner for 5 minutes. Following this cleaning procedure, a $SrTiO_3$ precursor sol was spin-coated over these substrates for 40 seconds at 4000 rpm under ambient air conditions. The substrates were placed on a preheated hot plate at 90ºC for 2 minutes after spin coating to remove the solvents and dry them. The samples were annealed in a furnace at 350ºC for 30 minutes after drying. After that, the thin film

was annealed at 750ºC for one more time. $SrTiO_3$ polycrystalline phase was obtained after 30 minutes of exposure to ambient air. A 300 mM SnO_2 solution was applied to the surface on top of $SrTiO_3$ coated p^{++}-Si substrate for semiconductor deposition at 3000 rpm, followed by a drying Process for 5 minutes at 90°C on a prepared hot plate. These dried samples were promptly annealed for 30 minutes in a preheated high-temperature furnace at 500°C, resulting in a polycrystalline SnO_2 film. Finally, a thermal evaporator was used to deposit the aluminum source and drain electrodes on top of the SnO_2 layer at a pressure of 6 x 10^{-6} pa, using a shadow mask with a W/L (23.6 mm/0.2 mm) ratio of 118. To test the capacitance and dielectric behavior of $SrTiO_3$ material, the thin-film device with a metal-insulator-metal (MIM) device structure was manufactured using comparable methods to those used for TFT production.

2.3.3 Fabrication of SnO_2 TFTs with $BaTiO_3$ as a dielectric-

The TFTs were built on a p^{++}-Si substrate that was extensively doped. The substrate was first ultrasonically cleaned before being treated with oxygen plasma. After that, the $BaTiO_3$ solution was spin-coated on Si substrates for 40 seconds at 4000 rpm, then annealed for 30 minutes at 350˚C. After that, another layer of $BaTiO_3$ solution was deposited and annealed for 1 hour at 850˚C. Metal-insulator-Metal (MIM) structure capacitor was made by evaporating Al on the surface of $BaTiO_3$ thin films to investigate their dielectric characteristics. The Al electrode had a length of 0.2 mm and a width of 23.6 mm. TFTs were made by spin-coating the SnO_2 precursor solution on the $BaTiO_3$ dielectrics and then annealing them for 30 minutes at 500˚C. Finally, the Al electrode was deposited using a shadow mask to create source/drain electrodes.

2.3.4 Fabrication of SnO_2 TFTs with bilayer TiO_2/Li_2SnO_3 as a dielectric-

Like earlier TFTs with PBZ gate dielectric, these TFTs were fabricated on top of a 15 mm x 15 mm heavily doped silicon (p^{++} -Si) substrate with a bottom-gated and top-contact device structure. Two different TFTs name Device-1 and Device-2 are two fabricated with Li_2SnO_3 and Li_2SnO_3/TiO_2 dielectrics, respectively. After the substrate cleaning process, a filtered precursor solution of Li_2SnO_3 dielectric was deposited over a clean p^{++}-Si substrate with a speed of 4000 rpm for 1 minute. After that, the samples were put on a heated plate at 90˚C to eliminate the solvent. Then, the samples were annealed in a high-temperature furnace for 30 minutes at 350°C. This procedure was repeated two more times to get the appropriate gate dielectric thickness. To obtain a crystalline coating of Li_2SnO_3, samples were annealed at 500˚C in the final phase of dielectric deposition. TiO_2 thin film was deposited before Li_2SnO_3 deposition for the TiO_2/Li_2SnO_3 bilayer dielectric. A precursor solution of TiO_2 (titanium butoxide, 300 mM) was spin-coated similarly and annealed at 500˚C for 30 minutes to get a crystalline thin TiO_2 layer. The Li_2SnO_3 dielectric was then deposited over the TiO_2 layer in the same way. The bilayer (TiO_2/Li_2SnO_3) dielectric thin film was then treated at 500˚C for 30 minutes to grow a compact bilayer crystalline thin film. A filtered solution of $SnCl_2$ (300mM) was spin-coated at 4000 rpm for 30 seconds over the dielectric thin film (Li_2SnO_3 or TiO_2/Li_2SnO_3) to deposit metal oxide semiconductor, followed by a drying and annealing procedure at 90˚C /1 minute and 500˚C /30 minute respectively to obtain a polycrystalline SnO_2 thin film. Finally, using a shadow mask approach, thermally evaporated aluminum source/drain electrodes (100 nm) were deposited, resulting in a TFTs device with a width-to-channel length ratio of 118 (W/L = 23.6/0.2 mm).

2.4 Material Characterization

To analyze the synthesized dielectric and semiconductor materials, as well as the produced thin films of respective materials, several material characterization methods were carried out. Out of them, thermal gravimetric analysis was performed for a detailed understanding of the thermal behavior of dielectrics material like crystallization temperature. An X-ray diffraction study was conducted for the structural analysis of our dielectric. UV-Visible spectroscopy was carried out to check the transparency level of our dielectric and semiconductor. Atomic force microscope and Scanning electron microscope were done for surface morphology study.

2.4.1 Thermal Gravimetric Analysis (TGA)-

The thermogravimetric analyzer (TGA) measures the rate of change in mass in materials with relation to temperature, such as dehydration, breakdown, and oxidation, over time and at different temperatures. If the material produces a gaseous component of the total mass of the material is reduced which gives several information about the thermal behavior of the materials. This may be a very useful tool for determining a material's thermal stability or probing its behavior in various environments. As a result, a Mettler Toledo thermogravimetric analyzer was used to test the thermal behavior of the produced materials (TGA). To maintain the environment neutral, nitrogen was employed for my samples. In the temperature range of 40 to 900˚C was set for this experiment and about 4 mg of sample was placed on the crucible with a scanning rate of 20˚C/min. As deterioration temperature, we used the temperature that corresponded to a 5% weight reduction. The same sample has also been used to determine glass transitions, crystallization, melting, and sublimation using differential thermal analysis (DTA), a thermo analytical approach. Based on the heat transfer between the source and

the sample, the differential temperature is plotted versus temperature, and the changes in the sample are displayed as either exothermic or endothermic.

2.4.2 XRD Analysis-

The identification of materials based on their diffraction pattern is one of the most common applications of XRD analysis. XRD provides information on how the real structure differs from the ideal one, in addition to phase identification. A Rigaku wide-angle X-ray diffractometer combined with a multi-temperature chamber and a graphite monochromator with a wavelength of 0.154 nm was used to analyze the X-ray diffraction of the produced powder samples. For thin film samples, we performed the Grazing-incidence angle X-ray scattering (GIWAXS) Measurement. At 45 kV and 200 mA, the generator worked. The samples were held on the sample holder, and the scans were carried out at a diffraction angle ranging from 2 to 80 degrees, with a scanning rate of 3 degrees per minute.

2.4.3 UV-Visible Spectroscopy for optical Analysis-

A UV-Vis spectrophotometer is a device that measures the absorption or transmittance of a material as a function of wavelength in the electromagnetic spectrum. In my Ph.D. study, I have used this instrument to determine the transparency of a sol-gel-coated dielectric thin film. For this, our dielectric was coated on a quartz substrate in the same conditions followed for device fabrication. The JASCO V-650 spectrophotometer was used to test the dielectric thin film UV-Vis spectroscopic properties within the wavelength range of 200-800 nm. We have also calculated the bandgap of semiconductors using the absorption coefficient data.

2.4.4 Atomic force microscopy for surface roughness analysis-

AFM is a strong Profilometry method for examining the surface topography of thin films. It provides quantitative data on surface and surface structure. It also investigates thin film surface microstructure. The morphological information of thin-film surfaces may be described via AFM imaging in terms of RMS roughness. In thin films, AFM is also used to investigate grain size and grain size distribution. In our case, the characterization of surface morphology of dielectric thin films is particularly important since the dielectric/semiconductor interface plays such an important role in the performance of thin-film transistors. Because the rough interface (dielectric/semiconductor) is known to function as a transport barrier and obstruct the flow of charge carriers in semiconductors, it is critical to creating a high-quality dielectric thin film with very low roughness. Because a charge carrier must expend more energy to cross the rougher surface's interface and effective carrier mobility of TFT is highly reduced. The bulk surface morphology of the materials was scanned using an NT-MDT multimode AFM (Russia), which was controlled by a Solver scanning microscope controller. The root mean square roughness of the sol-gel coated dielectric thin film is calculated using AFM's semi-contact mode. For the semi-contact mode, a 100 μM long single beam cantilever with a tip mounted with a resonant frequency range between 240 and 255 kHz and a spring constant of 11.5 Nm^{-1} was utilized.

2.4.5 Leakage current density measurement-

Before fabricating TFTs, it is necessary to characterize the dielectric thin film by measuring leakage current density. Because the dielectric thin film is placed between metal S/D electrodes and semiconductor channel and no current is expected to pass

through it. However, because of a few traces or pinholes present in the thin film and tunneling effect, a very low-level current flows through it in actuality. Using an Agilent B1500A semiconductor parameter analyzer, current-voltage density characteristics of MIM devices (p^{++}-Si/dielectric/Al) were measured in an open environment. **figure 2.2** depicts the configuration of the device construction.

2.4.6 Capacitance-frequency (C-f) measurements-

Another significant criterion to verify the viability of the insulating thin film used as a gate dielectric in TFTs is the frequency-dependent capacitance measurement of the dielectric thin film. For the C-f measurements have been done in the same MIM device structure. The dielectric constant of the employed dielectric layer in thin-film transistors is calculated using the capacitance value and thickness of the dielectric thin film. An LCR meter (Keysight LCR meter E4990A) was used to test the C-f of a device p^{++}-Si/dielectric/Al at frequencies between 100 Hz and 10 MHz while applying a 50 mV AC voltage.

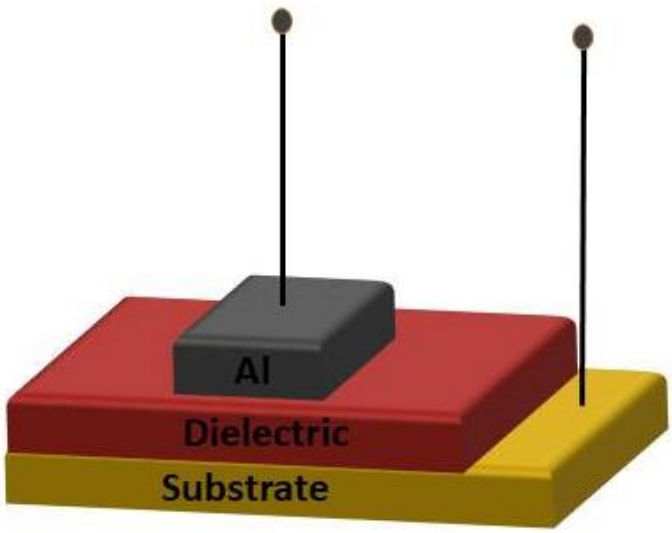

Figure 2.2: The Metal Insulator Metal device set up for C-f and I-V measurements

2.4.7 Thin film transistor characterizations-

The electrical characterizations of the TFT were studied in ambient atmospheric conditions. **Figure 2.3** depicts the TFT device's layout. There are two different types of TFT characteristics which are known as output characteristics and transfer characteristics. When drain current (I_D) of TFT is assessed concerning drain voltage (V_D) under constant gate voltage (V_G) (V_D vs. I_D) is called output characteristics. When I_D is assessed as a function of V_G variation under constant V_D, the features are referred to as transfer characteristics (I_D vs. V_G). The output characteristics are commonly used to ensure the TFT operation and its quality. This property describes the device's linear and saturation regions. The transfer characteristics, on the other hand, are more crucial since they provide the TFT's most critical device parameters, such as mobility, on/off ratio, and threshold voltage (V_T), among others. All of these TFT characterizations were placed in natural light. An Agilent B1500A semiconductor parameter analyzer was used to do the electrical measurements. Using a probe micromanipulators were used to make the electrical contact with the TFT. Using the gradual channel approximation, the electron mobility of TFT was calculated from the transfer characteristics.

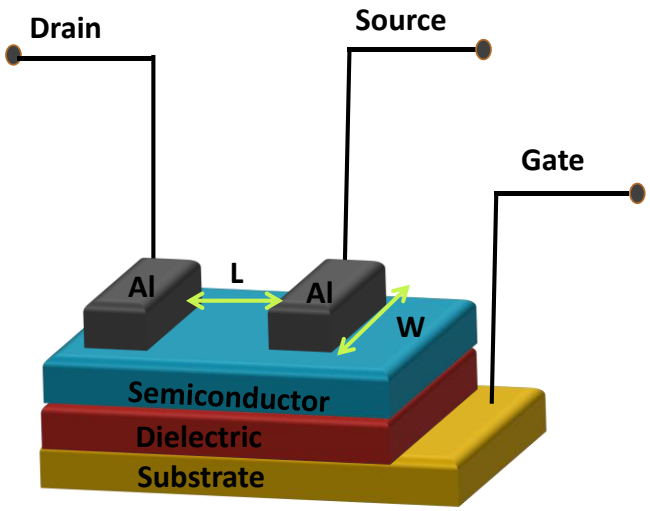

Figure 2.3: Bottom gate-top contact device setup for TFT characterization