Chapter 2

2.1 Materials synthesis

In this thesis work, two different class of metal oxide materials are synthesized by low-cost solution processed technique to fabricate metal oxide thin film transistor (TFT). One of them is ion-conducting oxide insulator that works as a gate dielectric of TFT and the other one is metal oxide semiconductor which works as an active channel of TFT. This solution processed technique is also known as sol-gel technique, enables the material to react uniformly at a molecular level and capable of producing a single compound polycrystalline thin film. Particularly in this synthesis process, we used metal salts which are dissolved in alcohol and used as dielectric or semiconductor details are given below.

2.1.1 Dielectric material Li_5AlO_4

The Li_5AlO_4 dielectric thin film was synthesized by sol-gel technique and successfully used as a gate dielectric for metal oxide TFT. We have used aluminum tri-secondary butoxide [$Al(OC_4H_9)_3$] and Lithium acetate (CH_3COOLi) as precursor materials. Initially, alumina sol with known concentration was prepared by the widely cited Yoldas process.[144, 145] A known concentration lithium acetate solution was also prepared by using 2-methoxyethanol (2-ME) solvent. After that, these two solutions were mixed with desired amounts to maintain Li and Al content with 5:1 ratio in the final ceramic product. The resultant solution was then stirred for 30 minutes at room temperature to prepare a clear homogeneous solution. This solution was then filtered through a syringe filter (0.45 μm) and was used for thin film dielectric fabrication on highly doped silicon (p^{++}-Si) substrate. A portion of the precursor solution was separated and was kept on a hot plate at

90 ^{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 diffractogram (XRD) and thermal analysis.

2.1.2 Dielectric material $LiAlO_2$

Similar to Li_5AlO_4, crystalline $LiAlO_2$ has been synthesized by the sol-gel technique that required much lower processing temperature than earlier. Particularly in this work, aluminum tri-secondary butoxide [$Al(OC_4H_9)_3$] and lithium acetate (CH_3COOLi) were used as the precursor materials for the synthesis of $LiAlO_2$. Firstly, alumina precursor sol of 300 mM was prepared by addition of an equal amount of 300 mM lithium acetate solution which was prepared in a 2-ME solvent.[144, 145] The ratio of two precursor solutions was taken such a way so that the ratio of Li and Al metal in the final ceramic product can be 1:1. For fabrication of the thin film samples, the resultant solution was spin coated followed by an annealing process. However, to prepare the powder $LiAlO_2$ sample, the solvent of the two precursors were removed and the remaining material was collected for annealing at various temperatures under the open atmospheric condition to obtain the crystalline powder of $LiAlO_2$.

2.1.3 Bilayer dielectric materials

To lowering operating voltage of TFT bellow 1.0 V, a semiconductor/insulator bilayer stacked dielectric has been used. The high permittivity semiconductor has been used in between the gate electrode and insulator. Particularly, TiO_2/ Li_5AlO_4 stacked dielectric has been used to fabricate indium zinc oxide (IZO) TFT. A 300 mM precursor solution of Al_2O_3 was prepared from aluminum nitrate nonahydrate ($Al(NO_3)$ $9H_2O$).by using 2-ME as the solvent and the solution was stirred for 4 hours to obtain a transparent sol. Similarly,

the precursor solution of Li_5AlO_4 with 300 mM concentration was prepared by mixing two individual solutions of lithium acetate and aluminum nitrate nonahydrate with a molar ratio of 5:1. The mixture was stirred for an hour at room temperature and in the ambient atmosphere to obtain a clear precursor sol of Li_5AlO_4. For TiO_2 deposition, a precursor solution of 100 mM was prepared by dissolving titanium butoxide in 2-methoxyethaol followed by a stirring process for 3 hours at 60 ^{o}C.

2.2 Semiconductor material IZO

Indium zinc oxide (IZO) has been synthesized by sol-gel technique and has been used as channel semiconductor for most of TFT reported in this thesis. For this metal oxide semiconductor synthesis, a separate 300 mM precursor solution of IZO was prepared. Reagent grade chemicals of indium chloride ($InCl_3$, 99%) and zinc acetate ($(CH_3COO)_2Zn$, 99%) in stoichiometric quantities were employed as starting materials. A measured amount of zinc acetate was dissolved in 2-methoxyethanol (2-ME) and stirred for 30 minutes at room temperature. Around 2% diethanolamine (99%) by volume was used as a stabilizer in this solution. Similarly, a separate solution of $InCl_3$ was dissolved in 2-ME as well. After that, both solutions were mixed with a molar ratio of 7:3 (In:Zn) and stirred vigorously for 2 hrs and used for deposition of the semiconductor layer in all the three types of TFT. These precursor solutions were filtered through a syringe filter (MVDF, 0.45µm) to remove the unwanted particles from the solutions before thin film deposition. Colloidal PbS quantum dot (QDs) of average particle size 5.6 nm has been synthesized by hot injection method.[146] For device fabrication, PbS QDs has been dispersed within octane with a concentration of 10 mg/ml.

2.3 Device fabrication

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

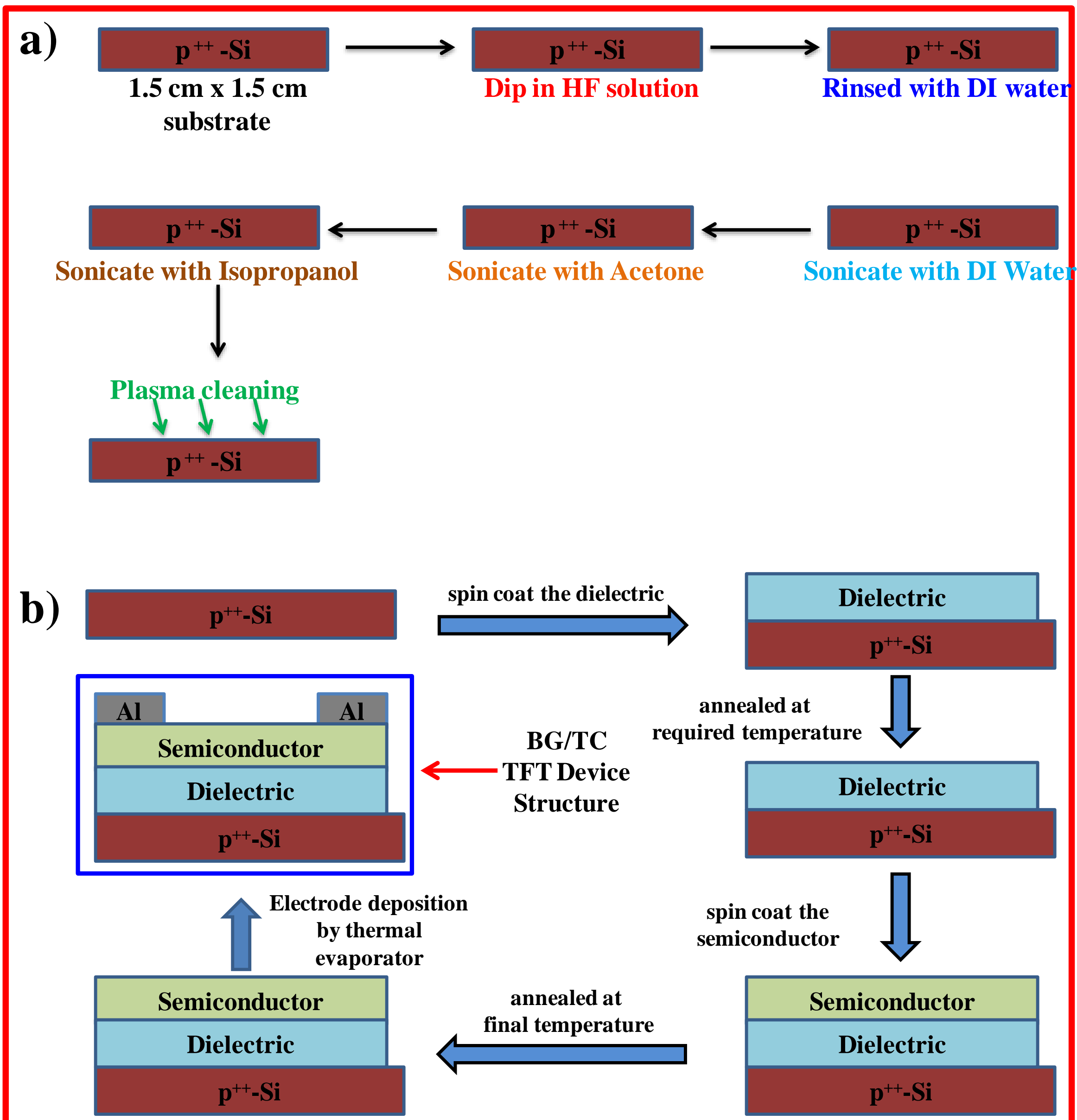

***Figure 2.1: a)** Flow chart of the cleaning process and **b)** flow chart of the device fabrication.*

2.3.1 For Li_5AlO_4 transistor fabrication

Initially, highly p-doped silicon (p^{++}-Si) wafers of 15mm×15mm size were immersed in hydrofluoric acid solution (HF: DI =1:10) for 2 minutes to remove the unwanted native oxides grown over the surface of the substrate and subsequently washed with DI water. After HF treatment, substrates were successively cleaned with four different solvents including soap solution, DI water, acetone and isopropanol by keeping inside an ultrasonic bath. After cleaning, wafers were dried by passing dry air and kept inside an O_2 plasma cleaner for 5 minutes to remove the organic substance and make it hydrophilic. Making a hydrophilic surface is very crucial for this sol-gel derived dielectric film fabrication as it enables the formation of a pinhole-free thin film with high uniformity. After this cleaning process, Li_5AlO_4 precursor sol was spin-coated over those substrates with a spinning speed of 2500 rpm for one minute under ambient atmospheric conditions. Immediately after spin coating, the substrate was kept on a preheated hot plate at 80 ^oC for 2 minutes to remove the solvents and make it dry. This process was repeated three times. Three different sets of substrates thus prepared were then annealed at 350 ^oC, 500 ^oC and 700 ^oC for 1 hour, 30 minutes and 30 minutes respectively under ambient atmospheric condition. Annealing at 350 ^oC decomposes all precursor salts to oxide and forms a very amorphous phase of Li_5AlO_4 (a-Li_5AlO_4) while annealing at 500 ^oC and 700 ^oC converted that precursor salts to fully crystalline Li_5AlO_4 which forms a polycrystalline ceramic thin film of Li_5AlO_4 on top of the p^{++}-Si substrate. Since Li_5AlO_4 is a wide band gap material[147], this polycrystalline film can act as a gate dielectric of a field effect transistor in which loosely bounded Li^+ can move up and down within the dielectric thin film and can form a vertically polarized film under external bias as depicted in Fig.-1a).[147-150] For metal oxide semiconductor

deposition, a 300 mM precursor solution of IZO was spin-coated on the top of Li_5AlO_4 coated p^{++}-Si substrate at a spinning speed of 4000 rpm. Immediately after spin coating, the substrate was kept on a preheated hotplate at 100 ^oC for 5 minutes followed by annealing at 500 ^oC in ambient atmosphere for 30 minutes to form a polycrystalline IZO film on Li_5AlO_4 dielectric layer. In the case of TFT with a-Li_5AlO_4 dielectric, IZO precursor film was annealed at 350 ^OC for 2 hours to maintain the amorphous phase of the dielectric. However, this annealing condition is good enough for high-quality IZO semiconductor fabrication.[151, 152] Finally, aluminum electrodes were deposited on top of the IZO film by using a thermal evaporator with shadow mask process to finish the TFT fabrication (Fig.-1b). For phototransistor fabrication, colloidal PbS QDs of concentration 10 mg/ml has been spin-coated on top of IZO-TFT with α-Li_5AlO_4 dielectric. After PbS deposition, 1% (by volume) 1,2-ethanedithiol (EDT) was deposited for cross-linking. These processes have been repeated for six times. The spinning speed of 2000 rpm was maintained throughout the deposition process. After six times coating, the thickness of the PbS layer becomes ~ 25 nm, which has been checked by AFM.

2.3.2 For $LiAlO_2$ transistor fabrication

Similar to an earlier set of TFT fabrication, all TFTs are fabricated on heavily p-type Si (p^{++}-Si) substrates of 15 mm x 15 mm size. Initially, all these substrates were cleaned in four different solutions as mentioned above. After the cleaning process, the spin coating of a $LiAlO_2$ dielectric precursor solution was carried out on top of these Si substrates at 3000 rpm for 1 minute in open atmospheric conditions. In order to fabricate the film with better quality, the precursor solution was filtered through MVDF -0.45μm before spin coating. All these spin coated films were placed on a hot-plate at 90 ^oC to remove the precursor

solvent quickly. These prepared substrates were annealed at 350 ^{o}C/3 hours, 500 ^{o}C/30 minutes, 700 ^{o}C/30 minutes respectively under ambient atmospheric conditions to form α-$LiAlO_2$, α-$LiAlO_2$, and β-$LiAlO_2$ dielectric thin films respectively. TFTs devices fabricated from these dielectrics are called **device-1, 2 and 3** respectively. The details of device fabrication summarized in **table 2.1.**

Table 2.1: *Fabrication details of device from $LiAlO_2$ dielectrics.*

Device	**Dielectric annealed $LiAlO_2$**	**Semiconductor annealed IZO**
Device-1	350 ^{o}C for 3 hours	350 ^{o}C for 3 hours
Device-2	500 ^{o}C for 0.5 hour	500 ^{o}C for 0.5 hour
Device-3	700 ^{o}C for 0.5 hour	500 ^{o}C for 0.5 hour

For device-1, IZO film was then annealed at 350 ^{o}C for 2 hours to form an amorphous IZO thin film. Whereas for two other devices, metal oxide semiconductor thin films were annealed at 500 ^{o}C for 30 minutes to grow crystallized IZO thin film on the dielectric layer. This higher temperature annealing conditions can generate a crystalline IZO thin film with a larger grain size that may give rise to higher carrier mobility. Finally, aluminum electrodes (source and drain) had been deposited on the top of the p^{++}-Si/$LiAlO_2$/IZO film in a thermal evaporator with shadow mask process to finish the fabrication of TFT.

2.3.3 Bilayer stacked dielectric fabrication

As mentioned earlier, for ultra-low voltage TFT fabrication, semiconductor/insulator stacked dielectric has been used. All these ultra low voltage TFTs were fabricated with a

bottom gate top contact device architecture by using different gate dielectric. A heavily p-doped silicon substrate (p^{++}-Si) was used as the substrate and also works as a gate electrode of the devices. At the beginning of TFT fabrication, all p^{++}-Si substrates were cleaned with HF successively in different solutions, as mentioned earlier. In this work, both the dielectric and semiconductor were deposited by spin coating process with a spinning speed of 4500 rpm under ambient atmosphere. After the spin coating, all these samples were kept on a preheated hot plate at 90 ^{o}C to eliminate the precursor solvent. For Li_5AlO_4/TiO_2 stack dielectric, a precursor of TiO_2 was spin coated on top of the clean p^{++}-Si substrate followed by an open atmosphere annealing process at 350 ^{o}C for 30 minutes to decompose the precursor salt into TiO_2 thin film. Subsequently, precursor sol of Li_5AlO_4 was spin coated on top of TiO_2 coated substrate in a similar manner, followed by an annealing process at 350 ^{o}C for 30 minutes. The spin coating process of Li_5AlO_4 precursor was repeated three times to achieve the sufficient thickness of the dielectric thin film. Finally, Li_5AlO_4/TiO_2 stack dielectric was annealed at 500 ^{o}C for 30 minutes to obtain a crystalline thin film. The Li_5AlO_4/Al_2O_3 bilayer dielectric was fabricated in a similar process by using the precursor sol Al_2O_3 and Li_5AlO_4, respectively. The devices with Al_2O_3, Li_5AlO_4, Li_5AlO_4/ Al_2O_3 and Li_5AlO_4/TiO_2 dielectric were named as **device-1, device-2, device-3 and device-4** respectively. After dielectric deposition, IZO semiconductor channel was deposited by another spin-coating and annealing process. In this deposition, a 300 mM precursor solution of IZO was spin coated on top of various dielectric layers with a spinning speed of 4500 rpm. After drying on the preheated hot plate (90 ^{o}C), all those samples were kept in a furnace at 500 ^{o}C for 30 minutes to form fully oxide IZO thin film. Finally, 100 nm aluminum source/drain electrodes were deposited by thermal evaporator under high

vacuum (10^{-6} m bar) through a shadow mask to provide a width to channel length ratio of 118 (W/L = 23.6 mm/0.2 mm). For capacitance and leakage current measurement, devices were fabricated in with a device geometry p^{++}-Si/dielectric/Al under the same condition. Similarly, for X-ray diffraction and atomic force microscope (AFM) studies, dielectrics were fabricated on p^{++}-Si by keeping the conditions the same that have been used for TFT fabrication.

2.4 Material characterization

Different material characterization techniques were used to characterize the synthesized dielectric and semiconductor materials and fabricated thin film of respective materials.

2.4.1 Thermal analysis

The thermogravimetric analyzer (TGA) gives the quantitative measurement of the rate of change in mass with respect to temperature in materials, e.g. dehydration, decomposition, and oxidation, with time and temperature. Mass is lost if the substance contains a volatile fraction. This can be a very powerful tool to examine the thermal stability of a material or to probe its behavior in different atmospheres. Hence, The thermal strength of the synthesized materials was checked with a Mettler Toledo thermogravimetric analyzer (TGA). Nitrogen was used to keep the environment inert. Approximately, 4 mg of sample was put on the crucible and scanned at the rate of 20°/ min in the temperature range of 40 to 900 ^{o}C. The temperature corresponding to 5 % weight loss was taken as degradation temperature. The same instrument has also worked as differential thermal analysis (DTA) which is a thermoanalytical technique to determine the glass transitions, crystallization, melting and sublimation. This differential temperature is then plotted against temperature

and the changes of sample are plotted as either in an exothermic or endothermic direction based on the heat flow between source and sample.

2.4.2 X-ray diffraction

X-ray diffraction of the synthesized powder and thin film samples was investigated using a Rigaku wide-angle X-ray diffractometer integrated with a multi-temperature chamber and a graphite monochromator using a Cu Kα source with a wavelength of 0.154 nm. The generator functioned at 45 kV and 200 mA. The samples were kept on the sample holder and the scans were done at diffraction angle from 2° to 80°, keeping the scanning rate 3°/min.

2.4.3 Fourier transform infrared spectroscopy (FT-IR)

FT-IR is one the most common and widely used spectroscopic method for the description of organic molecules based on the functional groups are present or not. The advantage of FT-IR spectroscopy over conventional spectroscopy is that it offers faster and high signal to noise ratio. Thermo-Nicolet 5700 FT-IR was used to record the infrared spectra of dielectric thin films taking the 100 scans with the resolution of 4 cm^{-1} in ATR mode.

2.4.4 UV-visible spectroscopy

UV-Vis spectroscopic measurement of the thin films of the dielectric was done using the JASCO V-650 spectrophotometer in the wavelength range of 200-800 nm. To check the visibility of sol-gel coated dielectric thin film, we used UV-visible spectroscopy.

2.4.5 Atomic force microscope

It's well known that the dielectric and semiconductor defect-free interface plays a very crucial role for high-performance TFTs, because carrier flows through a narrow region of

the channel through the dielectric/semiconductor interface. Therefore, the surface morphology of the solution processed dielectric thin film should be as smooth as possible for high device performance for BG/TC configuration. Hence, the surface roughness measurement of the dielectric thin film was studied with the powerful tool atomic force microscopic (AFM) with nanometer resolution. An AFM works in a different mode which depends on the distance between the tip of cantilever and sample surface. These different modes are namley contact mode, semi-contact mode and non-contact mode. This semi-contact mode eliminates the frictional force by intermittently contacting the surface and oscillating with sufficient amplitude to prevent it from being trapped in by adhesive forces. This mode of operation is less destructive than contact mode. The cantilever oscillates nearby its resonance frequency. An electronic feedback loop provides the oscillation amplitude remaining constant so that constant tip-sample interaction is conserved during the scan. The NT-MDT multimode AFM (Russia), controlled by a Solver scanning probe microscope controller, was used to scan the bulk surface morphology of the samples. Root mean square roughness of sol-gel coated dielectric thin film was calculated in semi-contact mode with this AFM. The semicontact mode was used with a 100 μm long, single beam cantilever on which a tip was mounted with a resonant frequency range of 240 to 255 kHz with the corresponding spring constant of 11.5 Nm^{-1}.

2.4.6 Leakage current density measurement

Leakage current density measurement is an important characterization of the dielectric thin film before the fabrication of TFT. Since we fabricate the sandwiched structure of the dielectric between two metal electrodes, ideally there should not any flow of current through the dielectric thin film. However, in practice, a very low-level current passes

through this because of a few traces or pinhole present in the thin film. With the help of this measurement, we can check the quality of the dielectric thin film and predict the order of leakage current when we use the same dielectric film use in TFT fabrication. Current-voltage density characteristics of MIM devices (p^{++}-Si/dielectric/Al) were performed under an open atmosphere using an Agilent B1500A semiconductor parameter analyzer. The layout of the device structure, as shown in **figure 2.2**.

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

Capacitance measurement of the dielectric thin film is another important parameter to check the feasibility of the dielectric used as a gate dielectric in TFTs. We fabricated metal plate capacitor MIM device structure for the C-*f* measurements. The effective area of the capacitor is the area of the mask used in the metallization of the top electrode. From the capacitance value, we calculate the dielectric constant of the used dielectric layer in thin film transistors. This C-*f* measurement has done with a devices p^{++}-Si/dielectric/Al by an LCR meter (Keysight LCR meter E4990A) at frequencies between 100 Hz and 10 MHz applying a 50 mV AC voltage. The layout of the device same as capacitance-frequency measurements structure is shown in **figure 2.2**.

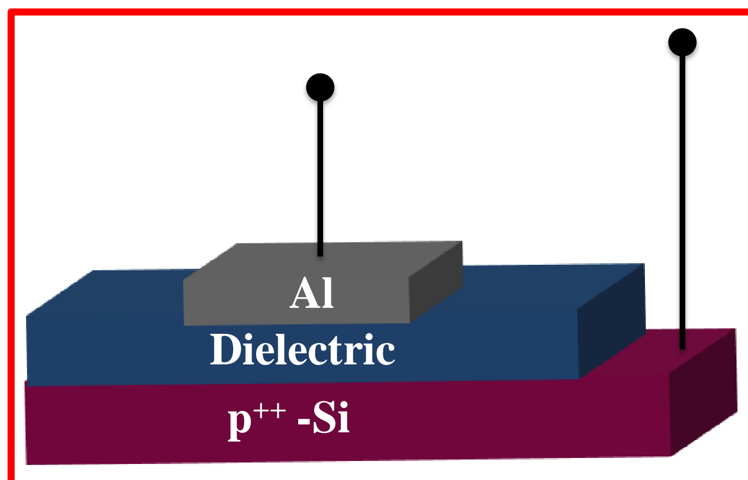

Figure 2.2: *Layout of the MIM device structure for C-f and I-V measurements.*

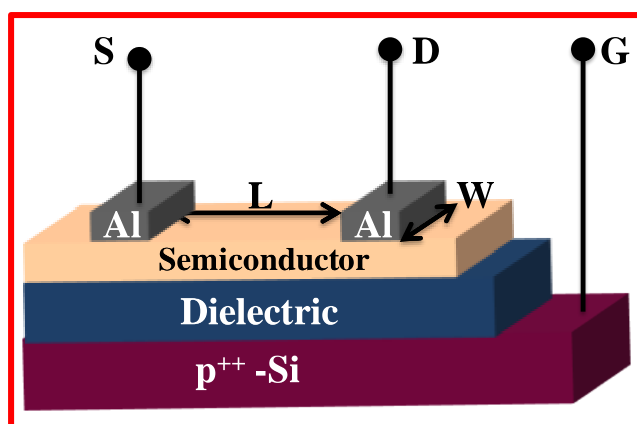

Figure 2.3: *Layout of the BG-TC device structure for TFT characterization.*

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 parameter of TFT including mobility, on/off ratio, V_{Th}, etc. All these TFT characterizations were performed in ambient atmospheric condition. 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.