

Chapter 2

MATERIALS AND EXPERIMENTAL METHODS

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2.1 Materials

2.1.1 Poly-3-hexylthiophene (P3HT)

Amongst the various organic semiconductors, Poly-3-hexylthiophene (P3HT) is an extensively studied and applicable organic semiconductor used in the fabrication of many potential organic electronic devices due to its good conductivity, solubility and environmental stability [Sirringhaus *et al.* (2005), Hamadani *et al.* (2004), Matsumoto *et al.* (2008), Assadi *et al.* (1988), Bao *et al.* (1996), Sirringhaus *et al.* (1998)]. The chemical structure of the P3HT is shown in the Fig. 2.1.

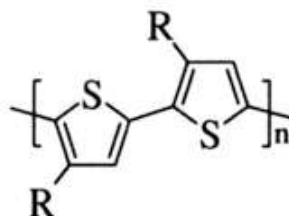


Fig. 2.1 Structure of P3HT

Synthesis of P3HT

Regioregular poly-3-hexylthiophene (RR-P3HT) was synthesized in the laboratory and the synthesis steps are given in Fig. 2.2. The technique followed in the synthesis of RR-P3HT has been previously reported [Seyler *et al.* (2013), Jeffries-El *et al.* (2005) Iovu *et al.* (2005)]. In the 1st step of synthesis, 20 ml LiCl/THF (providing 10 Mm LiCl) was mixed with 5 ml ter-BuMgCl/Et₂O (providing 2M ter-BuMgCl) and kept on magnetic stirrer for 5 to 10 min, in order to get a uniform solution. Dibromo-3-hexylthiophene (3.261 g) was added to this solution along with

chlorobenzene (Cl-Bz) for increasing the dilution of the solution to prevent precipitation. Further, the solution was stirred for 1 h at room temperature. To prevent precipitation, the solution was diluted with Cl-Bz during stirring. Yellow color concentrated activation (monomer) was obtained after 1 h.

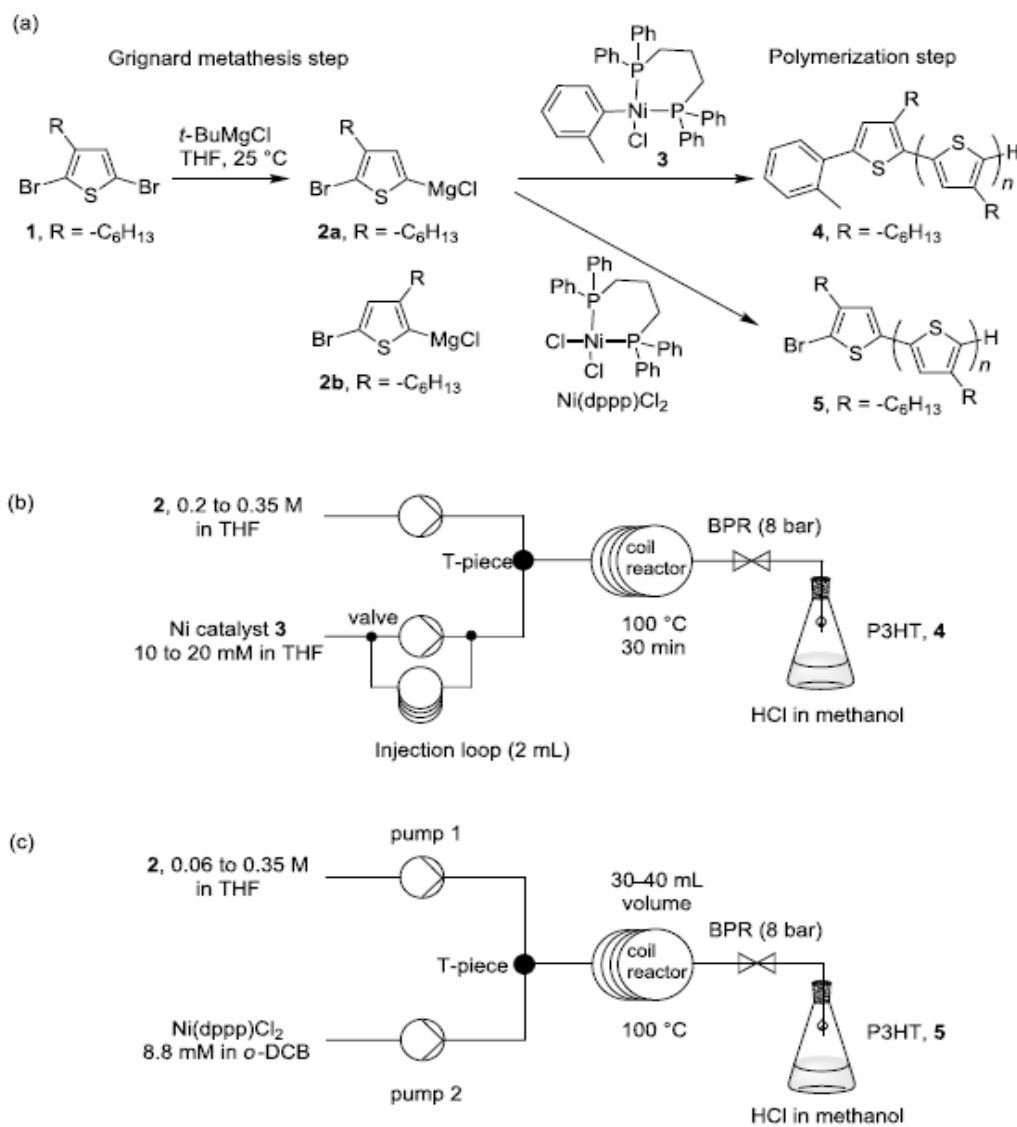


Fig. 2.2 (a) Preparation of thiophene Grignard monomer and synthesis of P3HT by Kumada catalyst transfer polymerization, (b) Schematic representation for the flow setup using nickel complex 3 and (c) Ni(dppp)Cl₂ [Seyler *et al.* (2013)].

Subsequently, Ni(dppp)Cl₂ (54 mg, 1 mol %) was dissolved in 2 ml CH₂Cl₂ and the whole solution was taken in a syringe and added in the main solution once, while keeping the main solution continuously stirring. Here, Ni(dppp)Cl₂ behaves as a catalyst (initiator) which initiates the polymerization reaction. The molecular weight of regioregular polymer depends on the amount of the catalyst which should be in the range of 1-5 wt%. In our case we used 1 wt% catalyst because, above 1 wt% we did not find good regioregularity. Optimum amount of the catalyst helps in regular polymer formation, otherwise random type polymers may be formed due to higher amount of the catalyst. Nearly 6 h later, color of the solution became dark purple and the total volume of polymerization solution was approximately 100 ml. This solution was further filtered (by using a vacuum pump) in a conical flask having 500 ml methanol (MeOH). The catalyst and un-reacted parts from the collected cake were removed by washing it with acetone using Soxhlet extraction method. Further, Soxhlet extraction was used to segregate the low-molecular-weight part from the obtained polymer by using hexane as solvent. At last, the residual parts were extracted by using chloroform to separate the un-dissolved part and dried in vacuum to obtain a fine black RR-P3HT powder [Tiwari *et al.* (2014)].

2.1.2 Graphene

Graphene is a continuous two-dimensional (2-D) sheet having all atoms at its surface. Each carbon atom of graphene is bonded with sp² hybridization such that it forms honeycomb structure. First time 2-D single layer graphene was prepared by separating it from graphite by using micromechanical cleavage, and this (graphene) was discovered by Novoselov, Geim, Morozov, Jiang, Zhang, Dubonos, Grigorieva and Firsov in the year 2004 [Novoselov *et al.* (2004)]. Graphene acts as basic elements for various graphite carbon allotropes; for example, 0-D carbon allotrope is

formed by the wrapping of graphene sheets, 1-D carbon allotropes such as nanoribbons, and carbon nanotubes (CNT) are built by rolling and slicing of graphene sheets, respectively, and 3-D carbon allotrope consists of graphene sheets stacked together such that each sheet is separated by 3.37\AA . Crystal structures of different carbon allotropes are shown in Fig. 2.3. Graphene shows various exclusive properties such as large theoretical specific surface area ($2630\text{ m}^2\text{g}^{-1}$) [Stoller *et al.* (2008)], excellent carrier mobility ($200000\text{ cm}^2/\text{Vs}$) and conductivity ($3000\text{--}5000\text{ Wm}^{-1}\text{K}^{-1}$) [Biswas *et al.* (2011)], good optical transparency ($\sim 97.7\%$) [Nair *et al.* (2008)], and high Young's modulus ($\sim 1\text{ TPa}$) [Lee *et al.* (2008)].

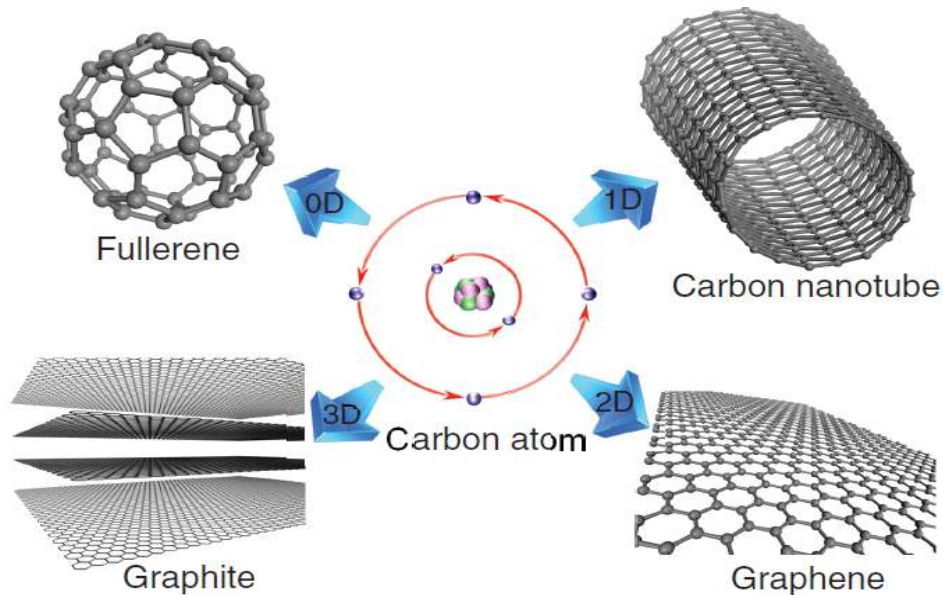


Fig. 2.3 Crystal structures of different carbon allotropes: Carbon atom consists of six protons and neutrons inside the nucleus, and two electrons revolve in the 1s orbital whereas the four other electrons are rotating in the next energetic 2s, 2p orbital (middle). The carbon atoms form 0D fullerene (top left), 1D CNT (top right), 2D graphene (bottom right), and 3D graphite structures [Biswas *et al.* (2011)].

These properties make it useful for several important applications such as light-emitting diodes, solar cells, transistors, radio-frequency (RF) electronics, and chemical sensors. Along with these unique properties, unfortunately, graphene

possesses some limitations such as, a few graphene growth methods require very high temperature (generally 1000 °C) and vacuum environment, that is very costly and hence, it might limit the large scale applications of graphene. The direct practical implementation of graphene in broad area organic electronic devices is confined due to number of reasons; first of all, the graphene sheet can easily get agglomerated in several organic solvents due to its hydrophobic nature [Lei *et al.* (2002)]. Secondly, its processibility is complicated, thirdly, it is not easy to control the number of several layers to peeled-off the fragments, and finally, it is a poor throughput process and unsuited for high scale production [Tiwari *et al.* (2014)]. Therefore, to overcome the limitations associated with pure graphene, it is preferred to use graphene as filler in few polymer, ceramic, or metal matrix in order to develop few hybrid nanocomposite materials. These composite materials possess superior mechanical, electrical and thermal properties compared to pure filler or matrix. It has been already reported that enhancement in electrical and mechanical properties of graphene-based polymer composites are much superior than other carbon filler based polymer composites [Stankovich *et al.* (2006), Ramanathan *et al.* (2008), Lee *et al.* (2009), Xu *et al.* (2009), Quan *et al.* (2009)]. Graphene and carbon nanotubes (CNTs) exhibit equivalent mechanical properties when used as nanofillers in some polymer matrix; however, graphene-composites exhibit superior electrical and thermal conductivity than CNT based composites. Performance of graphene/polymer nanocomposites firmly depends on the feature as well as the amount of graphene fillers to the polymer matrix. It also depends on the scattering of nanofillers, nature of chemical bond formed among the nanofillers and matrix, and fraction of nanofillers to the matrix. Pristine graphene is not well-suited to the organic polymers; therefore, it is difficult to form consistent composites with pristine graphene. On the

other hand, graphene oxide sheets are much friendly with organic polymers; therefore, graphene oxide works as excellent nanofiller for polymer nanocomposites.

In this work graphene used was purchased from Sigma Aldrich, USA. As graphene exhibits excellent carrier mobility, it was blended with P3HT in order to produce P3HT/Graphene hybrid nanocomposite material in order to increase the mobility of OFET.

2.1.2 Tetracyanoquinodimethane (TCNQ)

TCNQ is a strong electron acceptor organic material used for doping of organic semiconductors in order to enhance the electronic properties of organic electronic devices. In this work TCNQ used was purchased from Sigma Aldrich, USA. Doping with TCNQ promotes the formation of charge transfer complexes which improves the electrical conductivity of the doped film. Doping also increases the number of mobile carriers in the thin-film. Therefore, free charge carrier density of TCNQ doped P3HT film gets increased. Increasing doping concentration also increases the electric-field strength at the interface of electrodes (source, drain) and organic semiconductor which causes reduction in the ohmic contact (Au/doped P3HT) resistance [Zhang *et al.* (2010)]. Therefore, molecular doping of organic semiconductor with TCNQ improves the performance of an organic electronic device. The schematic chemical structure of TCNQ is shown in Fig. 2.4.

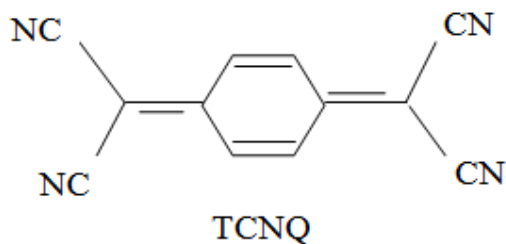


Fig. 2.4 Chemical structure of TCNQ

2.2 Experimental Methods

2.2.1 Steps for OFET fabrication

(a) Substrate preparation: Substrates for OFET fabrication were prepared in three steps,

- (i) Cutting
- (ii) Cleaning, and
- (iii) Surface modifications

(i) Cutting: The substrates of required dimensions (1 cm^2) were cut from a heavily p-doped silicon disc ($\text{p}^+\text{-Si}$) of thickness $500 \text{ }\mu\text{m}$ covered with thermally grown SiO_2 layer of thickness 300 nm shown in Fig. 2.5 (a). The capacitance (C_{ox}) per unit area of insulating layer SiO_2 was 10 nF/cm^2 . First, several cut marks of dimensions $1 \text{ cm} \times 1 \text{ cm}$ were drawn on the $\text{p}^+\text{-Si/SiO}_2$ disc by using diamond cutter, and then substrates (1 cm^2) were separated manually as shown in Fig. 2.5 (b). From one $\text{p}^+\text{-Si/SiO}_2$ wafer, approximately 50 to 55 substrates were prepared. Cutting should be done carefully as during cutting, silicon dusts get deposited which will damage the SiO_2 layer and create pinholes, thus allowing the flow of leakage current through the insulating layer and degrade the device performance fabricated on these substrates.

(ii) Cleaning: Silicon point dusts deposited on the substrates during cutting were removed from the fresh cut substrates surface by using hand blower. Then, all the substrates were treated in a mixture of aqueous solution of distilled water, hydrogen peroxide, and aqueous ammonia of a known ratio (2: 1: 1) for 1:30 h at $100 \text{ }^\circ\text{C}$ (Fig. 2.5 (c)). This treatment was done to remove the unwanted dust and other organic impurities from the surface of the substrates and provide hydrophilic SiO_2 surface having OH groups present at the surface. Finally, after

cooling the substrate at room temperature, they were washed again with distilled (DI) water and then dried using a blower.

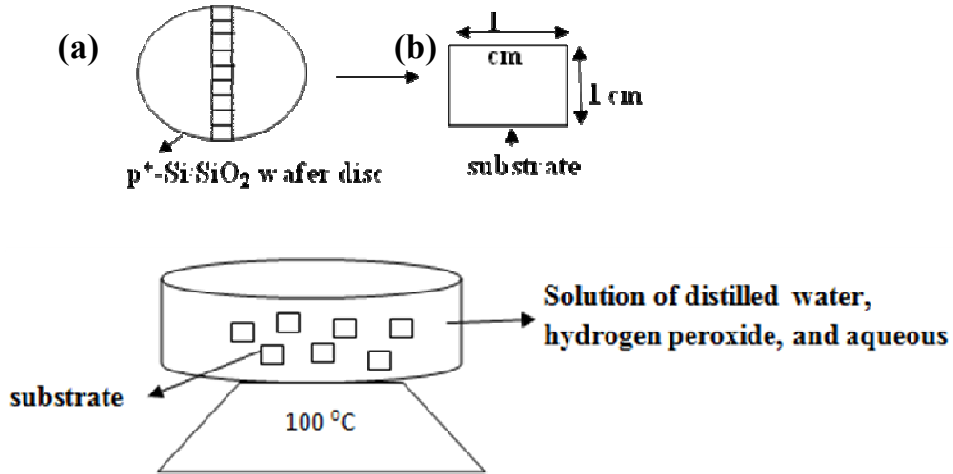
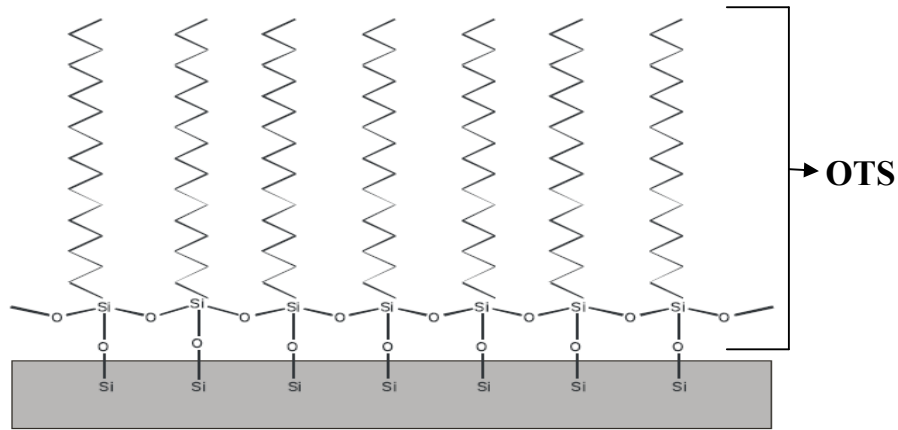
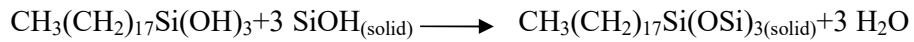
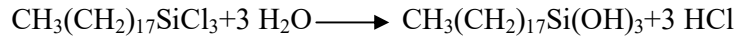


Fig. 2.5 (a) p⁺-Si/SiO₂ wafer disc, (b) substrate, (c) cleaning of substrates

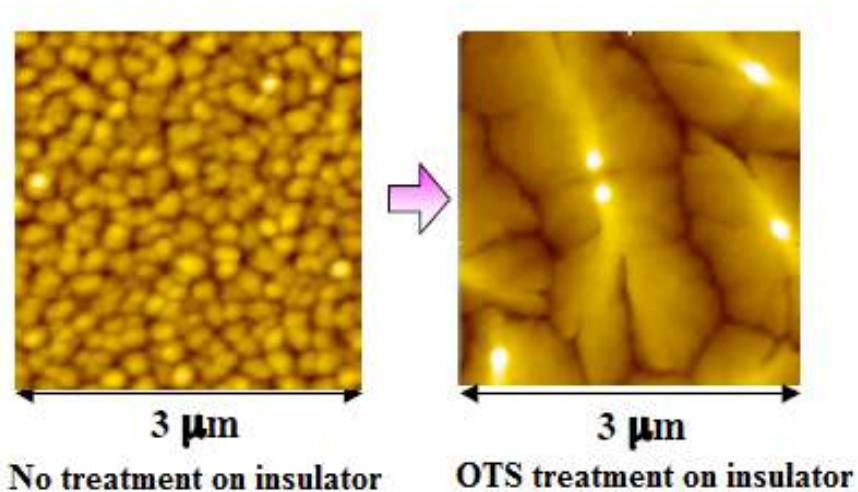
(iii) Surface modifications: Substrate surface modification is an important step of device fabrication. Modified substrate surface promotes the interaction among organic semiconducting thin-film and insulator layer. In order to modify the surface of the substrates (p⁺-Si/SiO₂) from hydrophilic to hydrophobic, all the substrates were treated in a mixed solution of dehydrated toluene and 2–3 drops of octyltrichlorosilane solution (OTS). This treatment was done for overnight (12–14 h). The chemical interaction amongst the surface of the substrates and octyltrichlorosilane molecules is shown in Fig. 2.6 (a). This treatment was done to enhance the smoothness of the surface and to provide hydrophobic surface which is very much compatible with the organic materials as they are also hydrophobic in nature. After removal from this solution, these substrates were further washed with dehydrated toluene, dried at 100 °C for 15 min, and finally stored in vacuum chamber. Surface treatment of insulator with OTS increases the

adhesion, grain size (shown in Fig. 2.6 (b)), thin-film uniformity and device performance (such as mobility).

The chemical reaction occurs between the surface of the substrate (SiO_2 layer) and octyltrichlorosilane molecules given by the equation (Fig. 2.6 (a))



(a)



(b)

Fig. 2.6 (a) Chemical reaction and interaction among SiO_2 and OTS molecules [Zhang *et al.* (2009)], **(b)** Grain size increases after OTS treatment

2.2.2 Semiconductor Thin-Film Deposition

Spin Coating

Spin coating is a very simple technique mostly used in laboratory for thin-film preparation of soluble organic conducting materials. In this study, homogeneous organic semiconductor (P3HT) solutions of known concentrations were prepared in chloroform and then deposited at the top of the p^+ -Si/SiO₂ substrates using this coating technique. Coating speed was maintained constant for all the devices fabricated in this study, and the spin coater used for thin-film coating is shown in Fig. 2.7. Initially coating speed was 1000 rpm for 10 s and then followed by 3000 rpm for next 50 s. During coating, the solution was spread at the top of the spinning substrate due to centrifugal force acting along it and the excess solution was thrown out from the substrate edge. Thin-film was formed after solvent evaporation. Thicknesses and the crystalline quality of the deposited thin-film can be controlled by controlling the concentration of the solution, solvent evaporation rate and spinning speed and time. Spin coated thin films showed good uniformity and reproducibility. The film thicknesses were estimated via DEKTAK 6M Profiler and thin-films morphology were studied using Atomic Force Microscopy (AFM).



Fig. 2.7 Spin coating unit

2.2.3 Thermal Annealing of the thin-film

The spin coated thin-film was further annealed at 80 °C for 1 h. Thermal annealing of P3HT thin-film is a very easy and efficient technique to improve the thin-film microstructure morphology and electrical properties. Device performance such as field-effect mobility gets enhanced significantly. Annealing of spin coated thin-film above the melting point or glass transition temperature of P3HT enhances the parallel π -conjugated orientation of P3HT molecules and crystalline nature of the thin-film which results in improvement of the electrical performance of the OFET.



Fig. 2.8 Picture of Furnace

2.2.4 Metal Electrodes (Source and Drain) Deposition

Two metal (Au) electrodes (source, and drain) of thickness 40 nm were deposited at the top of the coated thin-film using Ni-shadow mask by vacuum deposition method. The vacuum coating unit used in this study is shown in Fig. 2.9. Ni-shadow mask of defined dimensions as shown in Fig. 2.10 (a) were kept at the top

of the organic thin-film coated over the substrates (p^+ -Si/SiO₂), and then kept inside the thermal coating vacuum chamber. Gold wire was wrapped around the tungsten filament and then fixed properly at appropriate position inside the vacuum chamber. The pressure inside the vacuum chamber was maintained at approximately 4×10^{-6} torr. The gold deposition rate was maintained around 1 Å/sec. Evaporated gold molecules move in straight lines inside the chamber and then condense on the substrate. Deposition rate was controlled by regulating the temperature of the tungsten filament and film thickness was monitored with the crystal microbalance inbuilt in this coating unit. The channel length and width of the OFET device were maintained to be 20 μm and 2 mm, respectively. The schematic picture of the fabricated OFET is shown in Fig 2.10 (b).



Fig. 2.9 Vacuum coating unit (Model 12A4D)

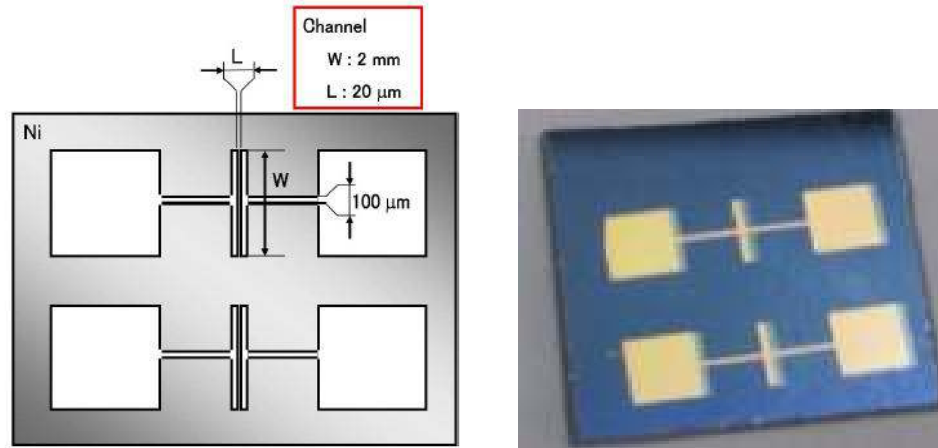


Fig. 2.10 (a) Schematic representation of the nickel mask used for the source and drain electrodes deposition [Arnaud *et al.* (2012)], **(b)** Image of the fabricated OFETs

2.2.5 Connections for three electrodes (Source, Drain, and Gate)

In order to connect the fabricated OFETs with measuring equipment, the OFETs were fixed in an acrylic box and the source, drain and gate electrodes of the devices were connected in an acrylic box by using thin copper wires of 0.1 mm diameter and silver paste as shown in the picture given in Fig. 2.11. Here, each chip has two OFETs and a common gate terminal for both devices. Several such chips were fabricated.

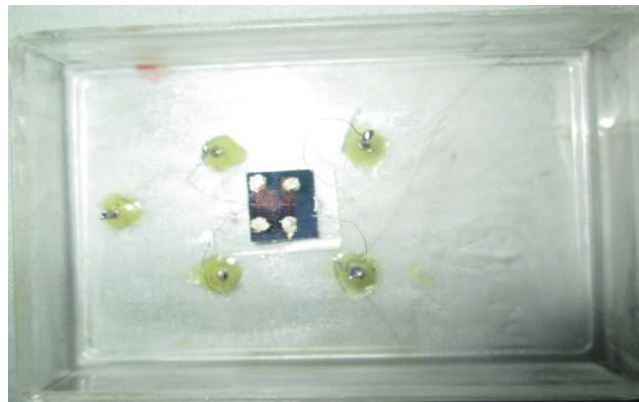


Fig. 2.11 Connection of three terminals of OFETs in an acrylic box by using silver paste and insulated thin copper wire

2.3 Characterization

2.3.1 Electrical characterization

The current-voltage (I-V) characteristics of the fabricated OFETs were measured by using Semiconductor Parameter Analyzer (Model No. Agilent B1500A) shown in Fig. 1.12, under proper vacuum condition. The three terminals of OFETs which was fixed in an acrylic box as shown in Fig. 2.11, were connected appropriately and then the chamber was pumped to get high vacuum of 10^{-6} torr. The I-V characteristics (output and transfer characteristics) of the transistors were measured in the vacuum. The drain or the output characteristic was measured for drain-source current (I_{DS}) verses drain-source voltage (V_{DS}) at a fixed gate-source voltage (V_{GS}), whereas, transfer characteristic was measured for I_{DS} verses V_{GS} at a fixed V_{DS} . The device parameters such as threshold voltage V_{TH} , field-effect mobility (μ), ON/OFF current ratio, transconductance (g_m), and subthreshold slope (SS) were extracted from these two characteristics.



Fig. 2.12 Semiconductor parameter analyzer (Model No. Agilent B1500A)

2.3.2 Atomic Force Microscopy

Atomic force microscopy (AFM) is an incredibly high-resolution scanning probe microscope. AFM is broadly used to study and measure the surface morphology of a material. AFM can measure the thickness of the solution coated thin-film. A key advantage of AFM is that it can provide true height as well as image of a non-conducting solid material without any coating. It has a cantilever along with a pointed probe (a few nanometers) which scans the sample surface point by point. AFM provides 3D image of a surface by measuring forces between the probe and the surface at very short distance. The probe smoothly gets in touch with the surface and records the small force acting amongst the probe and the surface. Generally, tapping mode is preferred for the surface characterization of a polymer thin-film in order to prevent from sticking of the probe with thin-film surface. In tapping mode of operation, the cantilever oscillates at or slightly close to its resonance frequency by a tiny piezoelectric crystal situated in the probe holder. The probe oscillates vertically, and the oscillation amplitude range is 20-100 nm. During oscillation, probe slightly touches the sample surface, and the interactions forces (van der Waals, electrostatic, dipole-dipole interactions) acting on the cantilever reduce the oscillation amplitude when the probe comes near the sample surface. This change is determined by a laser spot reflected through the top surface of the cantilever which is just above the probe into an array of photodiodes. A servo system thus adjusts the height to maintain a set of cantilever oscillation amplitude. The image obtained by an AFM in tapping mode is thus an image of the intermittent contacts of the tip with the surface [Arnaud *et al.* (2012)].