Chapter 6

6.1 Introduction

Two-dimensional (2-D) structure of graphene has numerous advantages over bulk semiconductors as a chemical gas sensor. A field-effect transistor (FET) based gas sensor with the bulk semiconductor is three-dimensional (3-D) in nature, where the variation electric charge changes over the surface of the channel could not always penetrate deep inside the channel of the device.[224, 225] This limits the sensitivity level of FET-based sensor devices. It is worth noting that GFET with the larger channel has a high surface area, can directly expose to the analyte or optical signal, and can create a large variation of drain current (I_D). Because of these reasons, a good number of works have been published on GFET-based chemical gas sensors[226, 227], biosensors[228], and photodetector.[229] Specifically, as a chemical gas sensor, graphene has been used to detect different hazardous analytes such as NH_3[230], NO_2[231], CO_2[232], etc. Among those, the NH_3 gas sensor has a great demand due to its wide uses in many applications, including refining, cleaning manufacturing, nitrogenous fertilizers, and refrigeration.[233, 234] Moreover, a long time expose of NH_3 is harmful to our eyes, skin, and breathing tract even with a low concentration of 1 ppm. In the last few years, research into graphene-based gas sensors has also be drawn a lot of attention.[235] To detect NO_2 at the ppm level[231], graphene preparation was explored by mechanical exfoliation of highly ordered pyrolytic graphite.[236] Though, the details about the charge transfer and behavior of gas sensing at open atmospheric conditions are still missing, which need further experimental exploration, especially in the use of Graphene field-effect transistors (GFETs). Moreover, most of those GFET have high operational voltage, low sensitivity with extensive temperature-dependent sensitivity.[230,

237] Besides, source/drain electrodes of all of these GFETs are fabricated by using photo or electron beam lithography, which are inherently expensive and low yield fabrication.[238]

To overcome all of these limitations, in this chapter, I have demonstrated a technique to fabricate large-area GFET that can provide good current saturation within 2V operating voltage. Sol-gel derives Li_5AlO_4 has been used as a gate dielectric of GFET that provided high capacitance to reduce the operating voltage of the device from 30-40 V to few volts. Whereas, chemical vapor deposition (CVD)- grown monolayer graphene has been used as the semiconductor channel of the transistor.[209] Source/drain electrodes of this GFET have been fabricated by thermal evaporation with shadow masking techniques with a channel length of as high as 0.45 mm. A control CVD deposition and precise transfer method of graphene capable us to fabricate a crack and discontinuity free large channel length GFET, which is a big concern of large-area graphene devices. The real device and schematic of device structure are shown in **figure 6.1 a)** and **b)**, respectively.

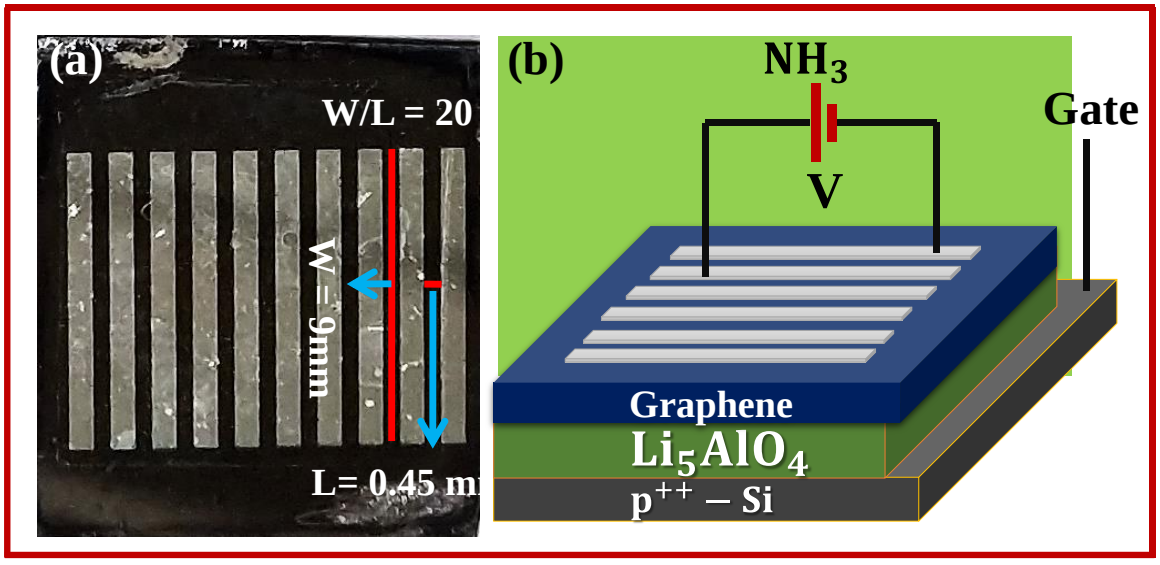

Figure 6.1: a) *Illustrating fabricated parallel electrode GFET Devices and* ***b)*** *schematic of the device with* p^+*-Si/*Li_5AlO_4*/Graphene/Ag/MoOx.*

6.2 Experimental

6.2.1 Method and Materials

Ion-conducting Li_5AlO_4 dielectric has been prepared by a sol-gel technique, which has been reported in our earlier work.[97] In this synthesis process, lithium acetate (CH_3COOLi) and aluminum tri secondary butoxide [$Al(OC_4H_9)_3$] have been used as precursor materials. Initially, a 300 mM concentration precursor sol of alumina was prepared by the Yoldas process, and lithium acetate solution of 300 mM was prepared separately by using 2-methoxy ethanol as solvent. Subsequently, both solutions were mixed with the preferred amount to maintain the ratio of Li and Al of 5:1 in the final ceramic product. The mixture was stirred for one hour under ambient atmospheric conditions to prepare a clear homogeneous solution and filtered through a syringe filter of diameter 0.45μm to remove the unwanted impurities (bigger particle) from the solution. After filtration, the precursor solution was ready to use as a gate dielectric for thin-film transistor fabrication. To measure the NH_3 gas sensitivity, a ½ liter ammonia gas cylinder has procured from sigma Aldrich.

6.2.2 Characterizations

Scanning electron microscope (SEM) (ZEISS, Germany), and transmission electron microscope (TEM) (FEI, USA) was used for detailed structural and morphological observations of graphene film. Raman spectrophotometer (Renishawin Via, Germany) equipped with a solid-state laser of wavelength 532 nm was used to determine the vibrational properties as well as to identify the number of layers present in the graphene film. Atomic force microscopy AFM (NT-MDT Service, Model No. NTEGRA Prima, with scan area 5 μm × 5 μm) is used to characterize the surface roughness of the dielectric of GFET. To determine the band gap of the dielectric, the 'UV-Vis absorption spectrophotometer' (Model No. SL-

164, Elico, India) was used. The Keysight make semiconductor parameter analyzer (B1500A) was used for electrical characterization. A manual probe station has been used to make contact with the electrodes of GFET.

6.2.3 Device Fabrication

This GFET has been fabricated with a bottom gate and top contact geometry, as shown in figure 1. The fabrication steps of this GFET are given bellow.

Step 1. The GFETs were fabricated on a heavily doped silicon (p^+-Si) substrate of dimension 15 mm x 15 mm. In the beginning, substrates were cleaned by soap solution followed by cleaning in three different solutions (water, acetone, and isopropanol) for 10 min each in an ultra-sonication bath.

Step 2. After this wet cleaning process, all wafers were dried by passing dry air and exposed by oxygen-plasma to eliminate undesirable organic material (hydrocarbons), which gathers on Si-substrate. The plasma cleaning process makes the substrates hydrophilic in nature. This is an essential step in sol-gel film fabrication because it allows us to deposit pin-hole free homogeneous thin film that effectively reduces trap states.

Step 3. After the plasma cleaning process, 300 mM precursor sol of Li_5AlO_4 was spin-coated on p^+-Si substrates at 5000 rpm for 45s under the ambient atmospheric condition and consequently kept on a hot plate at 90˚C for five minutes to remove the solvent and make the film dry.

Step 4. After the drying process, the sample was annealed in the furnace at 350 ˚C for 30 minutes. The same procedure was repeated two more times, and finally, all thin film samples

were annealed at 500 ^{o}C for 30 minutes under the ambient atmospheric condition to obtain polycrystalline α-phase of Li_5AlO_4.

Step 5. For an active channel of GFET, the graphene layer was deposited on the top of the Li_5AlO_4 layer by following the standard polymer assisted graphene transfer method.

Step 6. In the final step, silver (Ag) electrode (60 nm) with a molybdenum oxide (MoOx) interface (3 nm) was deposited on the substrate by thermal evaporation, a shadow-mask process under a pressure of 8.0 x 10^{-6} m Bar. The width (W) to channel (L) ratio of the device is 20 (W/L= 9 mm/0.45 mm).

6.2.4 Measurement Setup

The gas measuring set up consists of a chamber, temperature controller and humidity sensor, inlet, and outlet facility, and connection of different gas cylinders like; NH_3, O_2, N_2, and Ar **(figure 6.2)**. All the measurement was done at room temperature to ensure the ambient condition in the chamber, which is created by proving the mixture of 78% N_2, 20% O_2 and 2% Argon gases (or carrier gas) in the chamber. The measurement setup consists of a mass flow controller (MFCs), which controlled the flow of gases (5ml/min) and used to calibrate as per the required concentration. The temperature and humidity sensor has been attached to the chamber. Semiconductor parameter analyzer is used for recording the electrical data that mostly measured the variations of transfer characteristics in the presence of a low concentration of ammonia gas within the range from 0.1 ppm to 3 ppm. Gas-inlet and gas-outlet facilities are set on top of the channel of GFET, which is also an important factor to measure the transient response of the sensor.

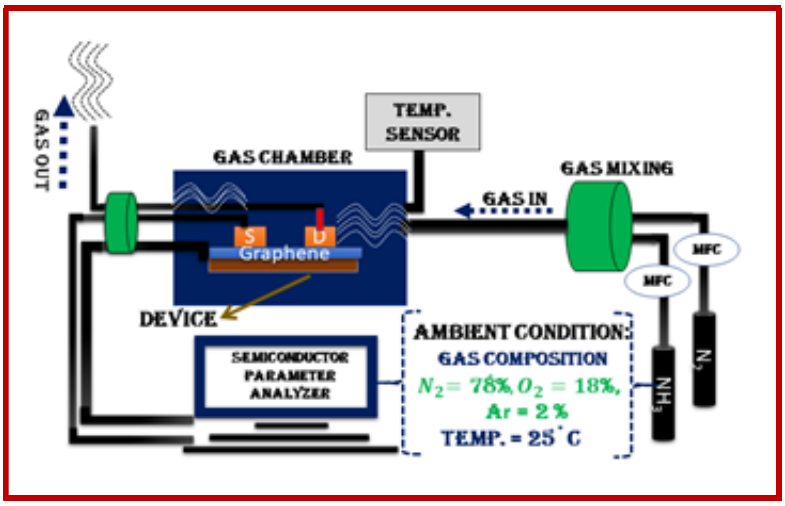

Figure 6.2: *Gas sensing experimental measurement setup.*

6.3 Results and Discussion

For Raman spectroscopy study, CVD grown graphene was transferred on a highly doped Si (p^+-Si) substrate, and the spectrum was recorded by using 532 nm laser excitation, which is shown in **figure 6.3 a)**. This study shows a prominent peak around ~1586 cm^{-1} and ~2680 cm^{-1}, which correspond to the G and 2D bands of graphene, respectively. Also, the intensity ratio of 2D and G band is found to be (I_{2D}/I_G) ~ 2.3, which confirms the presence of monolayer graphene in that particular region. Multiple measurements in different parts of the substrate show similar data that ensure the existence of monolayer graphene in a wide area of the substrate. The SEM image of the transferred graphene film is shown in **figure 6.3 b)**, which indicates that transferred-graphene is a continuous film with few wrinkles and defects which may have arrived during the synthesis and transfer process. For the TEM characterization, graphene film was transferred from Cu foil to a lacey carbon-coated TEM grid. The TEM image of graphene film shows continuous monolayer graphene with folded regions at the ends on a lacey carbon-coated TEM grid (**figure 6.3 c)**). A clear α-Li_5AlO_4 crystal formation has been identified through a grazing incident X-ray diffraction (GIRXD)

study, which is shown in **figure 6.3 d)**. The two intense peaks were identified due to the planes of reflection of (222) and (142). The band gap of Li_5AlO_4 was measured by the UV-Vis absorption spectra of α-Li_5AlO_4 film, which is shown in the inset of **figure 6.3 d)**, indicates it's the value of 5.4 eV. The root-mean-square (RMS) roughness of this Li_5AlO_4 is ~ 3 nm, which was obtained from the atomic force microscope (AFM) study, and those AFM images are shown in **figure 6.3 e)** and **figure 6.3 f)**.

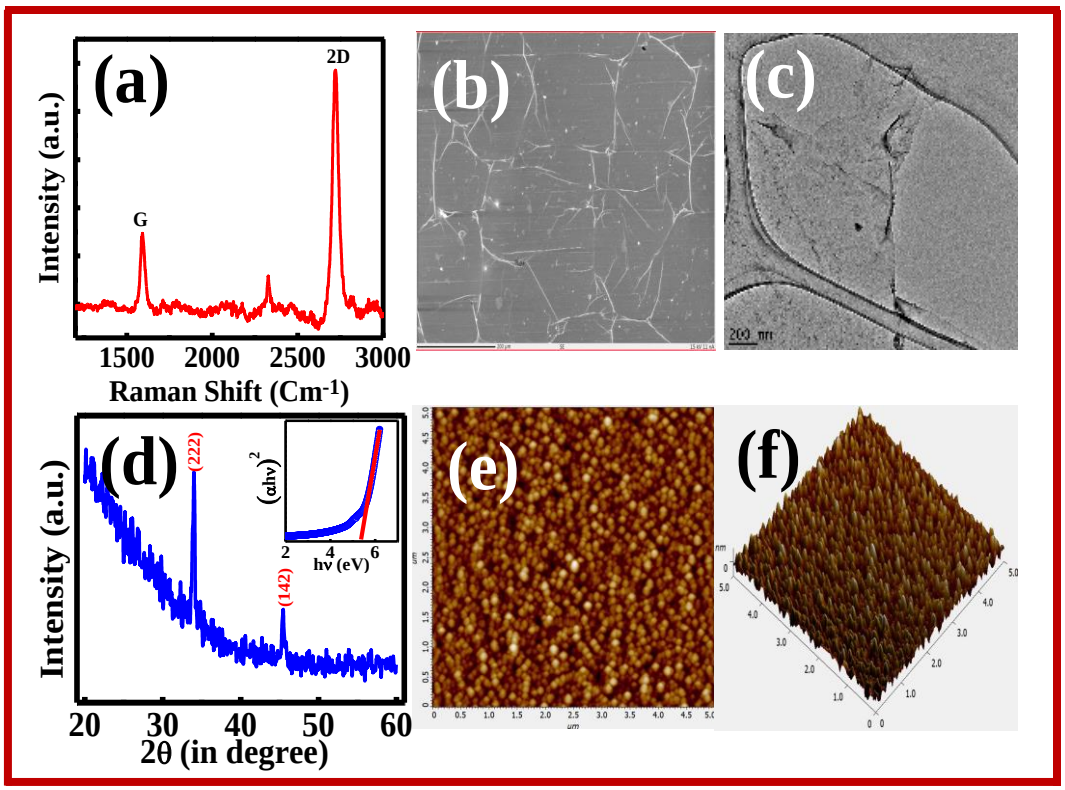

Figure 6.3: a) *Raman characteristics of the graphene sheet,* ***b)*** *SEM micrograph of the graphene sheet,* ***c)*** *TEM image of a graphene sheet on lacey carbon-coated TEM grid where lighter region corresponds to the monolayer graphene while darker region corresponds to the folded graphene layer,* ***d)*** *GIXRD (inset: UV-Vis absorbance spectrum)* ***e)*** *2D, and* ***f)*** *3D surface morphology of p^+-/Si/Li_5AlO_4 dielectric thin film annealed at 500* °C.

All electrical characterizations have been performed in ambient conditions. Capacitance and leakage current density of Li_5AlO_4 dielectric thin film were measured in a device structure of p^+-Si/ Li_5AlO_4/Al. The measured capacitance value of this dielectric thin film in various

frequencies (C-f) is shown in **figure 6.4 a)**, which indicates a capacitance value of the dielectric thin film is 318 nF/cm^2 at 50 Hz. Such a high capacitance of gate dielectric is responsible for fabricating low operating voltage transistor. The leakage current density-voltage ($J-V$) plot of Li_5AlO_4 dielectric is shown in **figure 6.4 b)**. This data shows a leakage current of 10^{-7} A/cm^2 at 2V, which is lesser compared to other dielectrics.[99] Also, there is no breakdown occurs of the device even at 20V operating voltage. These data suggested that this dielectric has low leakage current density and stable up to 20 V operations.

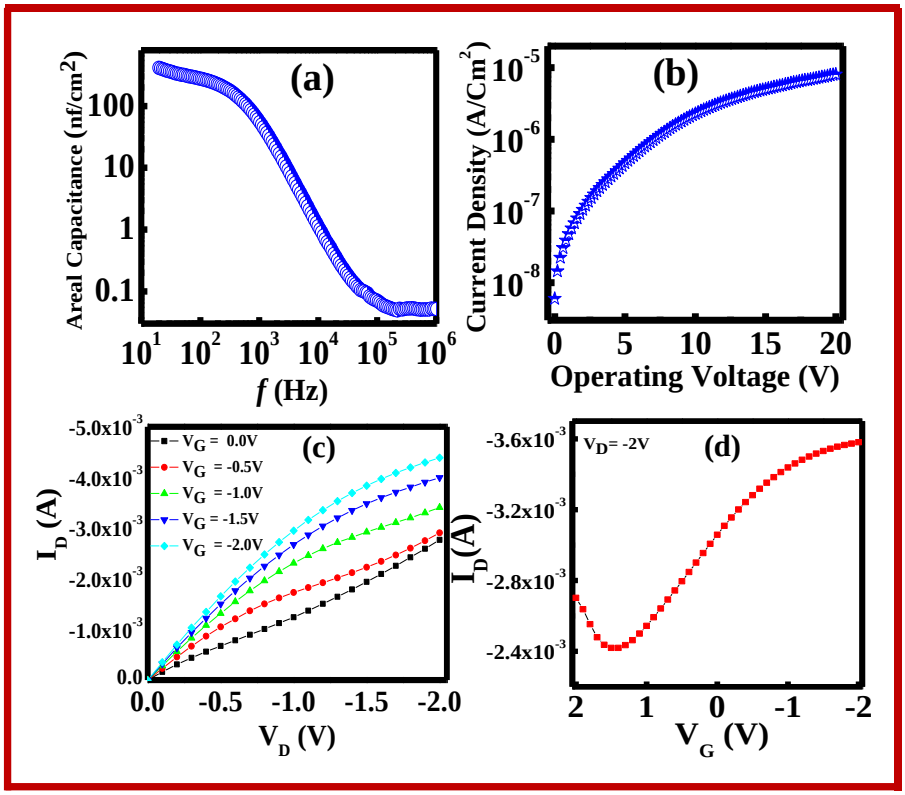

Figure 6.4: a) *C-f and,* ***b)*** *J-V characteristics of dielectric with the structure of p$^+$-Si/Li_5AlO_4 /Al,* ***c)*** *Output characteristics (I_D vs. V_D) and* ***d)*** *Transfer characteristics (I_D vs. V_G) of GFET.*

A low voltage operation output characteristics ($I_D - V_D$) of GFET have shown in **figure 6.4 c)** in which the drain voltage (V_D) was swept from 0 to -2V with a step size of 100 mV whereas gate voltage (V_G) was swept from 0 V to -2V with a 0.5 step size. The Li^+-ion

conducting dielectric, which provides very high capacitance, reduces the operating voltage of FET to 2V. Moreover, I_D it shows excellent current saturation even with a very large channel length (0.45 mm) of graphene. The transfer characteristics ($I_D - V_G$) of GFET were obtained by sweeping V_G from -2V to 2V at V_D of - 2V, as shown in **figure 6.4 d)**. For chemical sensitivity study, this GFET was kept inside a chamber of 10L volume with a facility of measuring, temperature, humidity, and with inlet-outlet connection for different gases. All these measurements were carried out in the ambient condition, i.e., with a gas mixture of 78% N_2, 20% O_2, and 2% Argon gases (or carrier gases) at 25˚C, in the chamber. The measurement setup consists of MFCs, which controlled the flow of gases (5ml/min) and used to calibrate as per the required concentration. Under this condition, transfer characteristics have been measured on various low concentrations of (NH_3) varied from 0.1 ppm to 3 ppm, which are shown in **figure 6.5 a)** and **figure 6.5 b)**. From this study, it is found that by increasing the amount of low ammonia concentration of NH_3, the Dirac point voltage (V_{dirac}) of GFET is shifted toward a more positive side. It is observed this shifting can be from 1.5V to 0.7V when NH_3 concentration changes from 0 to 3 ppm as shown in **figure 6.5 c)**. It's worth noting that our device carries a sufficiently large current in the range of mA, which is mostly due to majority carriers in the channel (holes for p-type). The NH_3 is a reducing gas analyte which acts as a strong electron donor (or hole acceptor). Hence, it can either be adsorbed with the top surface of the graphene channel or to the bottom of the graphene surface (i.e., Li_5AlO_4 dielectric). However, the second case has a very low chance of adsorption due to indirect interaction with ammonia gas. Since the ammonia gas has one lone pair of electrons, which has the tendency to interact with charge available for p-type semiconductors. When the reducing ammonia gas interacts with the graphene channel, the

transfer of lone pair of ammonia to the graphene molecule could lead to the depletion of holes in the channel, thereby reducing the current as ammonia graphene interaction. This current reduction is due to the enhancement of sheet resistance of the monolayer graphene channel.

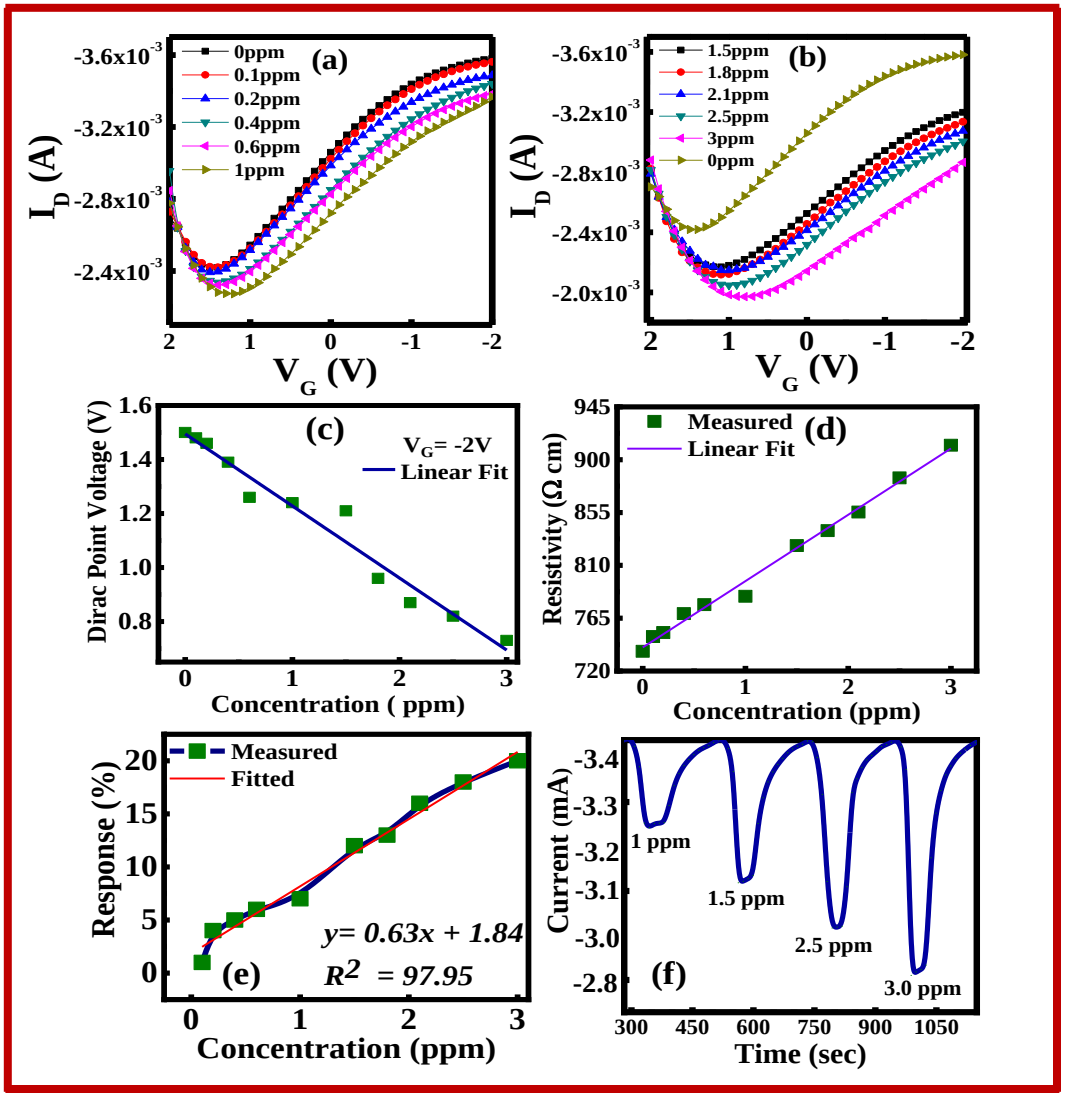

Figure 6.5: *Transfer characteristics in the presence of ammonia from* ***a)*** *0 to 1 ppm and* ***b)*** *1 to 3 ppm, respectively* ***c)*** *Variation of Dirac Voltage and* ***d)*** *change in resistivity with a concentration of gas,* ***e)*** *gas response and* ***f)*** *current vs. time response of ammonia gas sensor.*

Also, this GFET-based sensor has shown good linearity of variation of sheet resistance with the concentration of NH_3 (**figure 6.5 d)**) at 25˚C. At the same time, the response of the

device also has good linearity with a concentration of NH_3 gas (**figure 6.5 e)**) at room temperature. The transient response time study of this device indicates that the rise time is ~40 sec with a recovery time of ~120 sec (**figure 6.5 f)**). This data gives a clear sense of its real-time application.

6.4 Conclusions

High-k dielectric Li_5AlO_4 has been successfully utilized as a dielectric for the bottom gate GFET fabrication, which provides a very high capacitance value of 318 nF/cm^2, low leakage density of 10^{-7} (at 2V) with a high breakdown voltage (>20V). The single graphene layer, which was grown by the CVD method, has a very high uniformity that has confirmed by SEM and TEM study. Using this CVD grown graphene and ionic dielectric, large area GFET has been fabricated with a channel length of 0.45 mm that required only 2 V gate voltage to obtain good drain current saturation. Moreover, solution-processable dielectric and lithography free shadow masking fabrication can reduce the fabrication cost of the device to a very large extent for 2D based GFET. The highly invasive NH_3 gas sensing has been investigated for stable GFET in ambient conditions. The interaction of ammonia gas on the graphene channel showing a very good sensitivity (~20%) at room temperature even at a very low concentration (1 ppm) of ammonia exposure. The average response time and recovery time is found to be ~40 sec and ~120 sec, respectively. Large change in Dirac point variation from 1.4V to 0.7V, showing the highly sensitive ammonia-based GFETs.