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High-performance Hydrogen Sensor Based on Reverse-biased MoS_2/GaN Heterojunction

6.1 INTRODUCTION

The ever increasing energy demand and depletion of traditional fossil fuels ignited a spark for the exploration of new alternative energy resources. Among various alternatives, hydrogen is one of the cleanest sources of energy for meeting the futuristic energy demands. Hydrogen can widely be used in generating electricity, creating fertilizers for agriculture uses, and fuelling in space applications. However, the transformation from conventional energy sources to hydrogen involves many challenges. Even the very small concentration of hydrogen possesses serious threat of explosion due to its flammable nature(Cracknell et al., 2002). According to the NFPA standard, hydrogen is having a rating of four out of four on the flammability scale. Further, hydrogen is odorless and colorless, which makes its detection very difficult. Thus, detecting and monitoring of hydrogen gas is the stringent requirement because of safety concerns. In our research work, we have demonstrated a very high-performance hydrogen sensor to detect any leakage while storing, delivering, and using hydrogen gas.

Over the last decade, the semiconductor gas sensors have drawn a huge interest for monitoring and detecting of various environmental pollutants, since the adsorbed gas molecules can easily be detected by a change in current/resistance upon exposure of gas(Chhowalla et al., 2015; Chhowalla et al., 2013; Donarelli et al., 2015; Ou et al., 2015). Beyond conventional semiconductors, two-dimensional TMDs have generated significant interest due to its potential application for field-effect transistors, photodetectors, biomedical engineering, solar cells, and nanoelectronic devices(Liu and Liu, 2018; Lopez-Sanchez et al., 2013; Tsai et al., 2014; Yoon et al., 2011). MoS_2, the torchbearer of TMDs family, has opened up new avenues for sensing applications due to its distinct material properties, including large surface-to-volume ratio, low power consumption, swift charge transport process, and built-in flexibility(Kang et al., 2017; Ko et al., 2016).

Recently, mixed dimensional semiconductor heterojunctions have been recognized as an essential building block to create solid-state devices(Jariwala et al., 2017; Xu et al., 2017). In particular, the 2D vdW heterojunctions offers a powerful platform for high-performance gas sensing applications by harvesting the individual advantages of different materials(Huang et al., 2017; Um et al., 2016; Yeh et al., 2017). A large number of 2D heterojunctions have already been explored for their suitability in multifunctional sensing operations. MoS_2 based vdW heterojunctions have emerged as a promising candidate due to their appealing attributes, such as their dangling-bond-free surface and easily tunable junction properties(Gong et al., 2014; Jariwala et al., 2015). By forming heterostructures, the researchers exploited the new functionalities of MoS_2 not only in optoelectronic and energy harvesting devices but for various potential sensing applications also. MoS_2 plays a crucial role in sensing operation due to its very large surface-to-volume ratio, thus making the MoS_2 based heterostructures highly sensitive to gas molecules(Cho et al., 2015; Wu et al., 2017). A large number of such heterojunctions have been found suitable for molecular sensing due to their high sensitivity, excellent gas-sensing stability, and the simple sensing mechanism. A comparative analysis of popular gas sensors using metal oxide and 2D heterostructures has been shown in Figure 6.1.

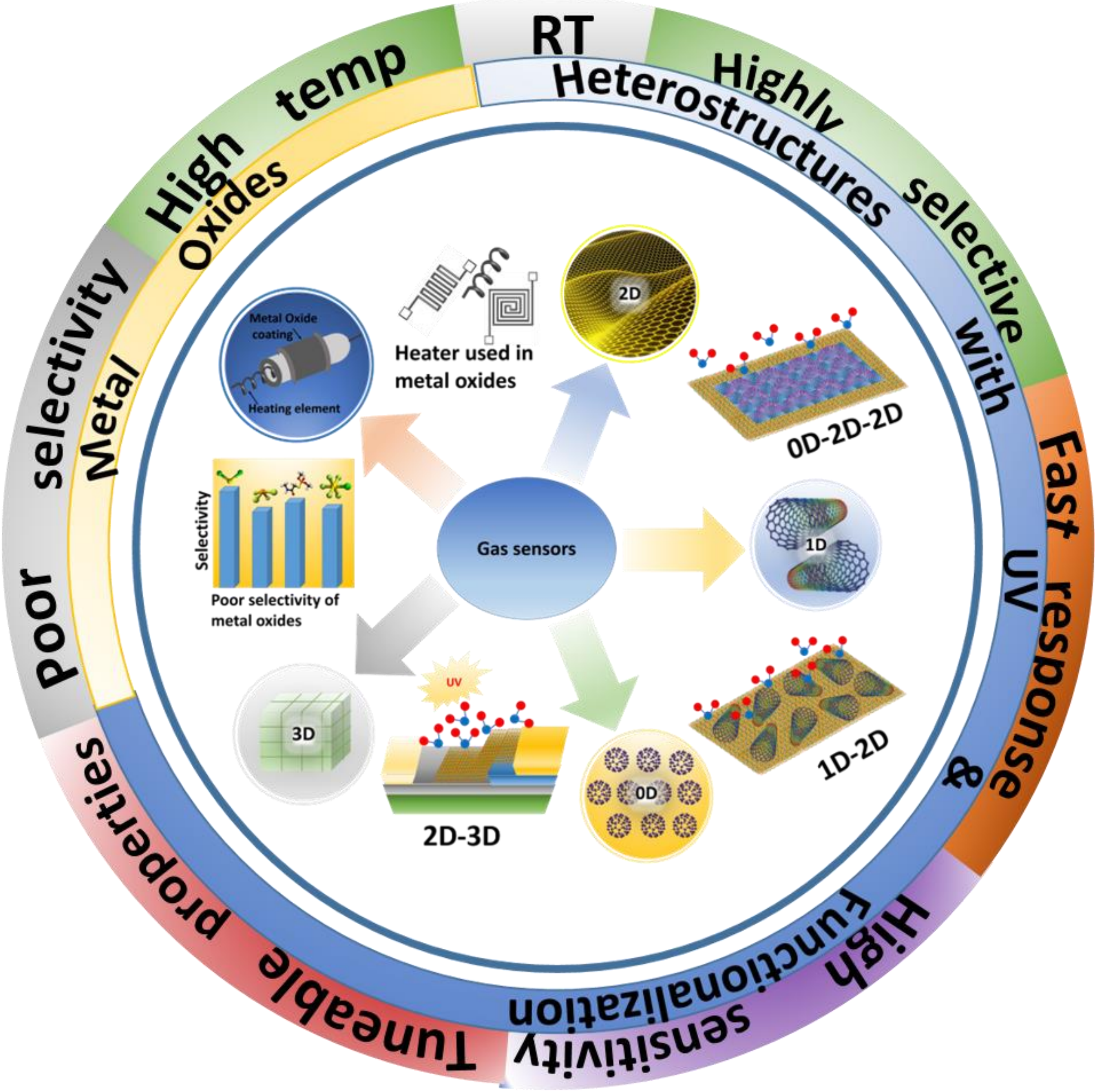

Figure 6.1: A comparative analysis of popular gas sensors using metal oxide and 2D heterostructures.

In particular, the MoS_2/GaN heterostructures have great potential not only for optical sensors but equally attractive for gas sensing applications also(Cho et al., 2015; Ruzmetov et al., 2016). Our previous endeavors include exploring the ultraviolet photodetection capability of MoS_2/GaN heterojunction for high-performance optoelectronic devices(Goel et al., 2018). However, no sincere efforts were made to study the MoS_2/GaN heterojunction for sensing applications. The existing reports of MoS_2/GaN heterojunction explored only the optoelectronic relevance, and the study of promising sensing applications remains untouched. Moreover, in all the existing reports, either mechanical exfoliation or CVD technique was used. Mechanical exfoliation method of MoS_2 results in a high crystalline and excellent structural integrity. However, this method yield is very low, which makes it unsuitable for practical applications(Magda et al., 2015). Sincere efforts were made to increase the yield by using other methods, for instance, by CVD using multiple precursors and by surface treatment, but results in irregular film thickness and low carrier mobility(Kuru et al., 2015).

6.2 EXPERIMENTAL DETAILS

6.2.1 Fabrication of MoS_2/GaN heterojunction

The fabrication process of MoS_2/GaN has already explained in earlier chapters. We have used the same two step procedure, sputtering coupled with sulfurization process in a sulfur rich environment. The fabrication procedure of MoS_2/GaN heterojunction is shown in the flowchart (Figure 6.2).

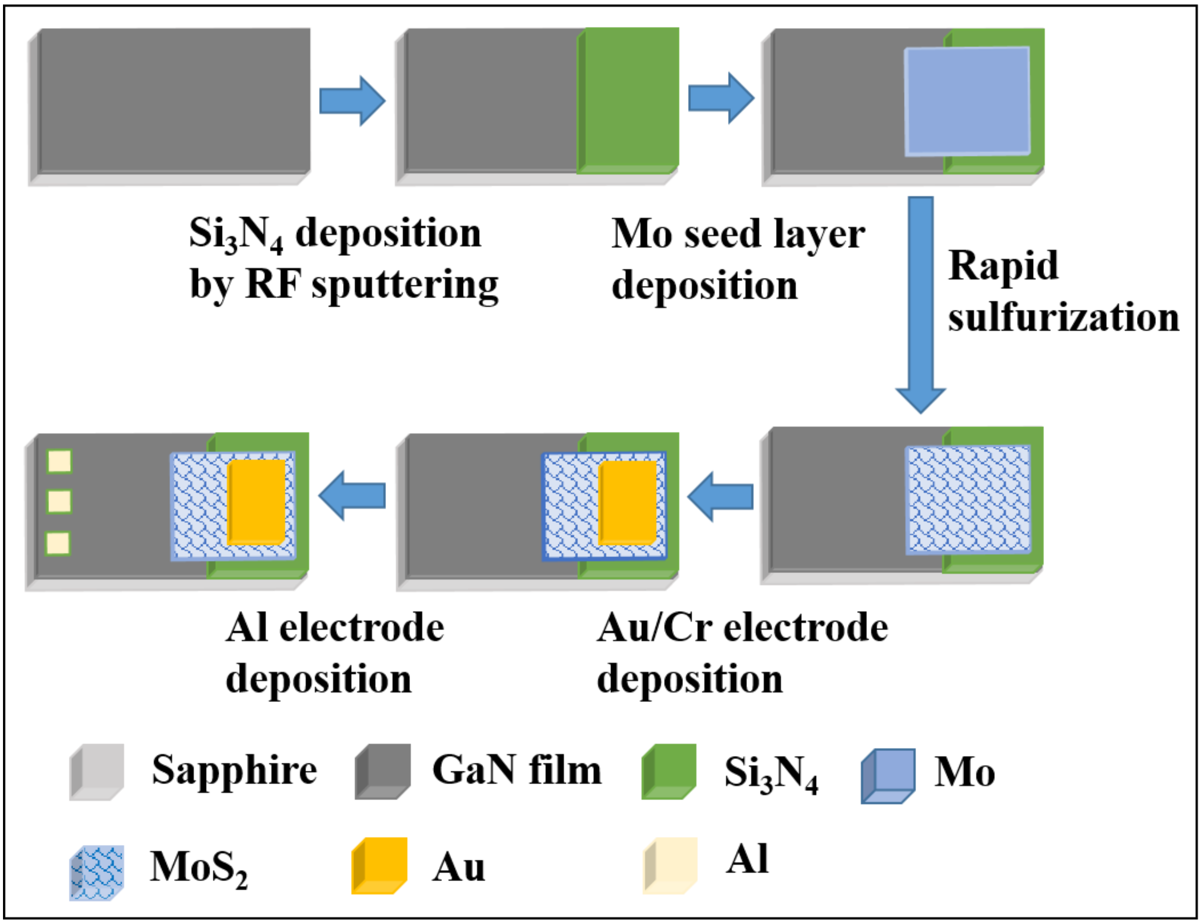

Figure 6.2: Fabrication flowchart of MoS_2/GaN heterojunction gas sensor.

6.2.2 Gas sensing measurement

The Gas-sensing behavior of the MoS_2/GaN heterojunction was examined by exposing the device with 0.1% (1000 ppm) to 5% (50000 ppm) hydrogen concentration. The temperature of the device was raised up to 180 °C using an external heating filament. Here, change in resistance of the devices upon gas exposure was measured by Keithley 4200 semiconductor characterization system using the relation R=V/I at a fixed voltage bias of –3V.

6.2.3 Characterization of MoS2/GaN heterojunction

A schematic illustration and the optical image of the fabricated MoS_2/GaN heterojunction are shown in Figure 6.3(a and b). Further, to examine the thickness and structural quality of the as-grown MoS_2 film, we performed several other microscopic and spectroscopic measurements, explained in the chapters 4 and 6.

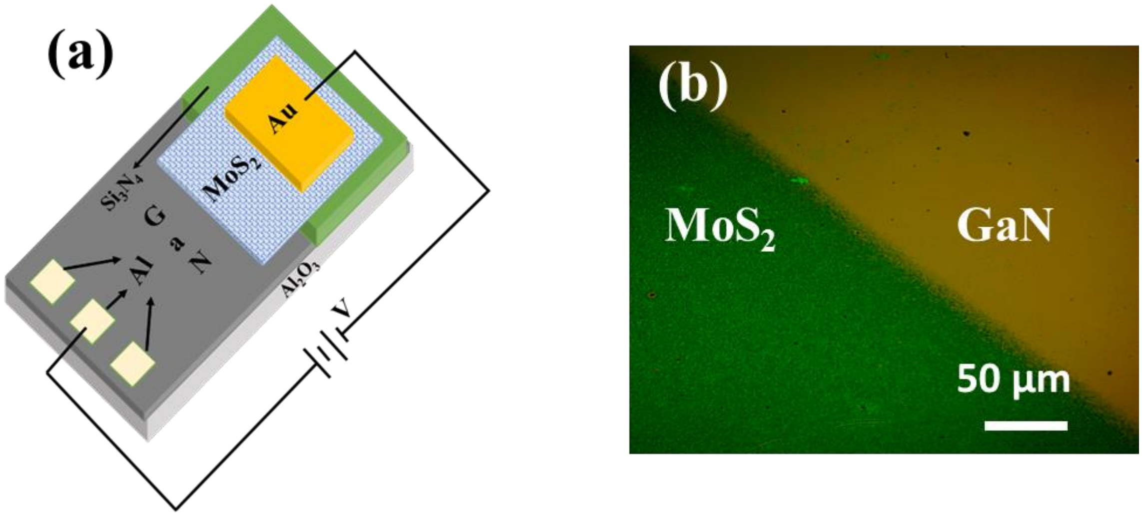

Figure 6.3: (a) Schematic diagram of the fabricated device. (b) optical micrograph of at MoS_2/GaN heterointerface, affirming the large-scale growth of MoS_2 on GaN substrate.

6.3 SENSING PERFORMANCE OF MoS2/GaN HETEROJUNCTION

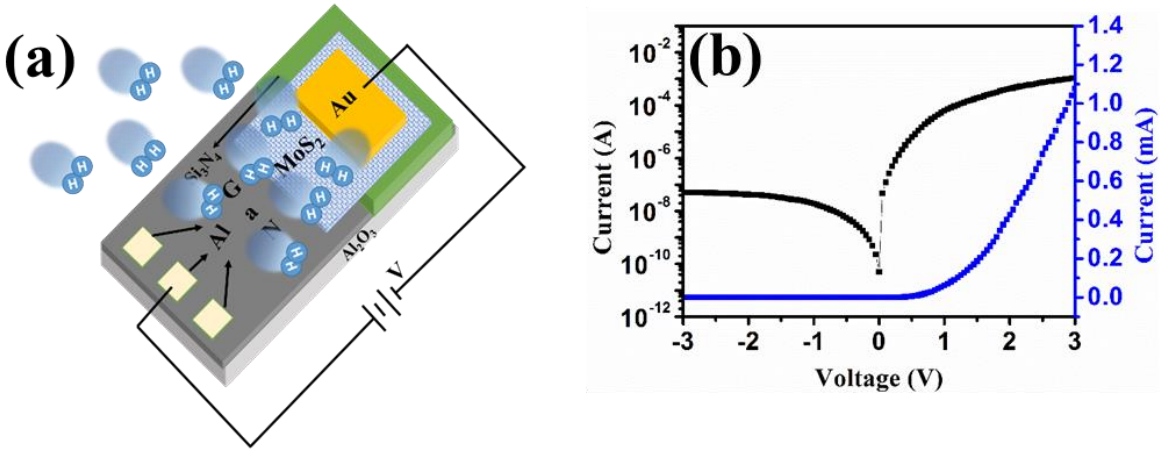

Figure 6.4: (a) 3D schematic illustration of the MoS_2/GaN heterojunction based sensor under hydrogen molecules. (b) Current-voltage characteristics of MoS_2/GaN heterojunction using log and linear scale at room temperature.

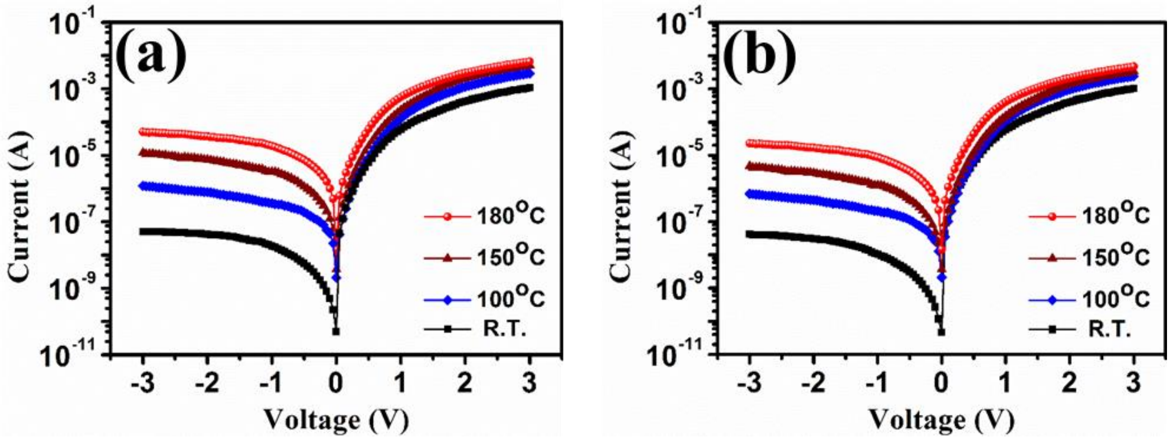

Figure 6.5: (a) Current-voltage characteristics of MoS_2/GaN heterojunction measured at different temperatures in (a) absence and (b) presence of hydrogen.

Figure 6.4(a) shows the schematic illustration of the MoS_2/GaN heterojunction based sensor under hydrogen exposure. To study the behavior of the fabricated device, the electrical characterization was done at room temperature, as displayed in Figure 6.4(b). The Au makes a low-resistance contact with MoS_2, and Al makes an ohmic contact GaN. Therefore, the rectifying behavior primarily originates from the MoS_2/GaN heterointerface(Radisavljevic et al., 2011; Roul et al., 2011). Figure 6.5(a) shows the I-V characteristics of the device measured at different operating temperatures (25-180 °C). All the measured I-V characteristics exhibit rectifying behavior. However, rectifying behavior dampened with an increase in operating temperature. This dampening behavior is due to thermally induced electrons at a higher value of temperatures, which increases the carrier density at the MoS_2/GaN heterojunction. With the increase in temperature, the I-V characteristics inches closer to the ohmic behavior.

Hydrogen molecules are physisorbed on top of Mo atoms (T_M), S atoms (T_S), hexagon (H), and Mo-S bonds (B) and perturb the charge density in MoS_2 through electronic charge transfer between hydrogen gas molecules and different adsorption sites(Yue et al., 2013). Additionally, Li et al. have demonstrated the dissociative adsorption of hydrogen molecules on MoS_2 surface through first principle calculation(Li et al., 2016). The unsaturated Mo atoms due to the presence of sulfur vacancies saturate after making bond with disassociated hydrogen atoms. Upon dissociation of hydrogen on MoS_2, the two H atoms form bonds with different Mo atoms with a bond length of 1.698 A˚ and 1.865 A˚. When we put our sensor under hydrogen exposure, the current at the MoS_2/GaN heterojunction decreases in both the forward and reverse direction because the hydrogen captured the electrons from the MoS_2 film (Figure 6.5(b))(Agrawal et al., 2017). After careful inspection of Figure 6.5(a and b), we noticed that upon hydrogen exposure, the decrease in current in the reverse direction is more prominent as compared to the forward direction. The decrement in reverse current inches the I-V characteristics back to the rectifying behavior even at a higher value of temperature (150 °C).

Figure 6.6(a-d) shows that the dynamic response resistance of the sensor with different concentrations of hydrogen at varying temperatures (25-180 °C). The response of the sensor was characterized for 0.1% (1000 ppm) to 5% (50000 ppm) hydrogen concentration. The results indicate that the resistance of the sensor increased with the increase in hydrogen concentration. A cycling test was performed of the MoS_2/GaN heterojunction gas sensor to 1% (10000 ppm) hydrogen at 150 °C, as shown in Figure 6.6(e). The sensor illustrates a highly reproducible and stable sensing behavior over the repeated test cycles. The gas sensitivity was measured as $(\Delta R/R_0) \times 100\% = (R_g - R_0)/R_0 \times 100\%$, where R_g and R_0 are the resistance of the sensor in presence and absence of gas, respectively. It was observed from Figure 6.6(f) that the relative response and hence the sensitivity increases with an increase in sensing temperature, and it reaches a maximum value at 150 °C. The sensitivity values of MoS_2-only and GaN-only films obtained from dynamic response resistance curves of Figure 6.8(a and b) have also been added in Figure 6.6(f) as control samples. An increase in sensitivity at the heterojunction is due to S vacancies, which are formed at the edge sites during the growth of MoS_2 film(Agrawal et al., 2017). The DFT calculation showed that adsorbed ambient oxygen molecules on S vacancies of MoS_2 have a strong binding energy of ~2.395 eV(Nan et al., 2014). It is well known that oxygen adsorbed into sulfur or defect sites on the MoS_2 surface through chemisorption and physisorption processes. The removal of chemisorbed oxygen from MoS_2 surface requires a high value of energy owing to strong hybridization between oxygen and MoS_2 orbitals. However, physisorbed oxygen atoms could easily be desorbed from the MoS_2 surface due to weak adsorption energy and a small amount of charge transfer(Qi et al., 2016). Qiu et al. have also removed the oxygen by 43% after annealing the device at ~80 °C in vacuum(Qiu et al., 2012). Therefore, removing physically adsorbed ambient oxygen leads to generating new active sites, which lead to increased adsorption of hydrogen molecules. Thus, the sensitivity of the device increases with an increase in temperature up to 150 °C. Moreover, sensitivity decreases beyond 150 °C due to different adsorption and desorption activation energies. At lower temperatures, the adsorption phenomenon is more prominent as compared to the desorption process due to the lower value of activation energy. Thus, up to a temperature of 150 °C, the adsorption phenomenon prevails. However, beyond 150 °C the desorption process became more effective resulting in decrement in sensitivity. Additionally, the excessive generation of high energy thermally induced charge carriers at a temperature above 150 °C also led to drop in sensitivity(Wei et al., 2009). The theoretical detection limit of our MoS_2/GaN based sensor was calculated to be 1.244 ppb.

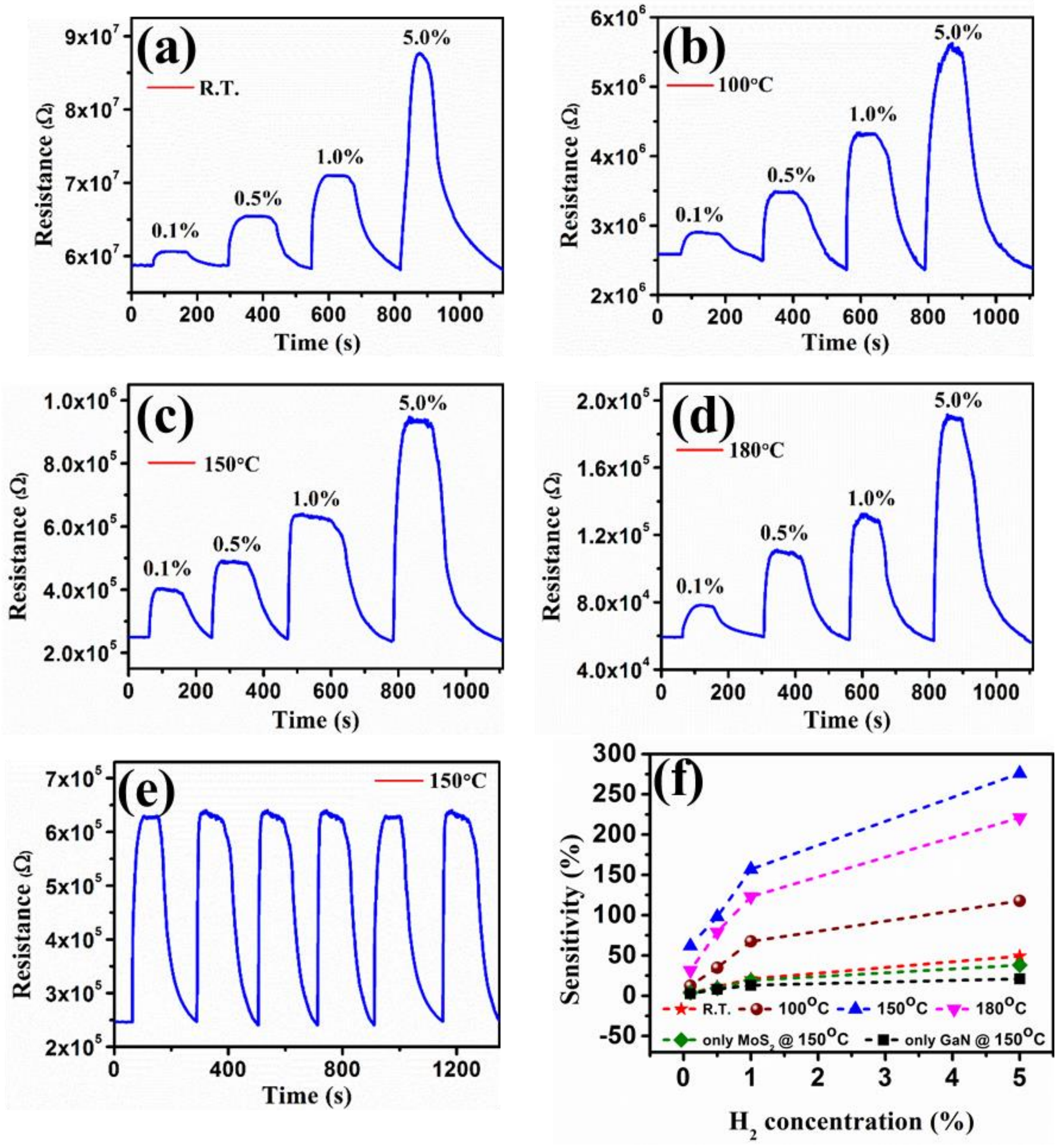

Figure 6.6: Dynamic response resistance to different concentration of hydrogen at (a) R.T., (b) 100 °C, (C) 150 °C, and (d) 180 °C. (e) Cyclic test with 0.1% hydrogen concentration at 150 °C. (f) The sensitivity of the MoS_2/GaN sensor as a function of hydrogen concentration at different values of temperature. The sensitivity curves of MoS_2- only and GaN only at an optimum temperature of 150 °C have also been added as control samples.

6.4 SENSING PERFORMANCE OF INDIVIDUAL MoS2 AND GaN FILMS

The I-V characteristics of the only-MoS_2 film with Cr/Au contacts and only-GaN film with Al contacts in presence and absence of different concentration of hydrogen at an optimum operating temperature 150 °C is shown in Figure 6.7(a and b). Upon hydrogen exposure, a little change was observed in the I-V characteristics. The dynamic response resistance of only-MoS_2 and the only-GaN film was depicted in Figure 6.8(a and b). At 1% hydrogen exposure, a sensitivity of 18% and 12% were measured for only-MoS_2 and only-GaN film, respectively, which is orders of magnitude lower than the heterojunction based devices. Thus the higher sensitivity must originate from the heterojunction between MoS_2 and GaN.

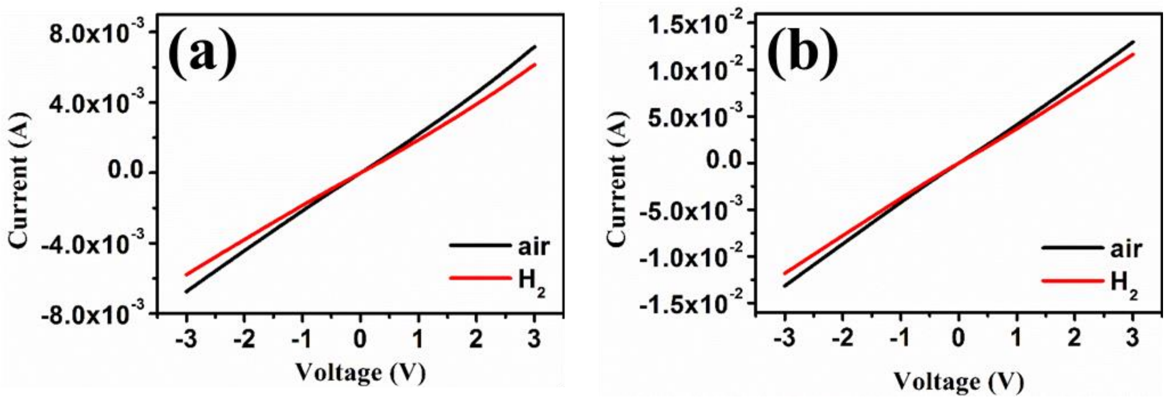

Figure 6.7: I–V characteristics measured in absence and presence of 1% hydrogen at 150 °C for (a) only MoS_2 film (b) only GaN film.

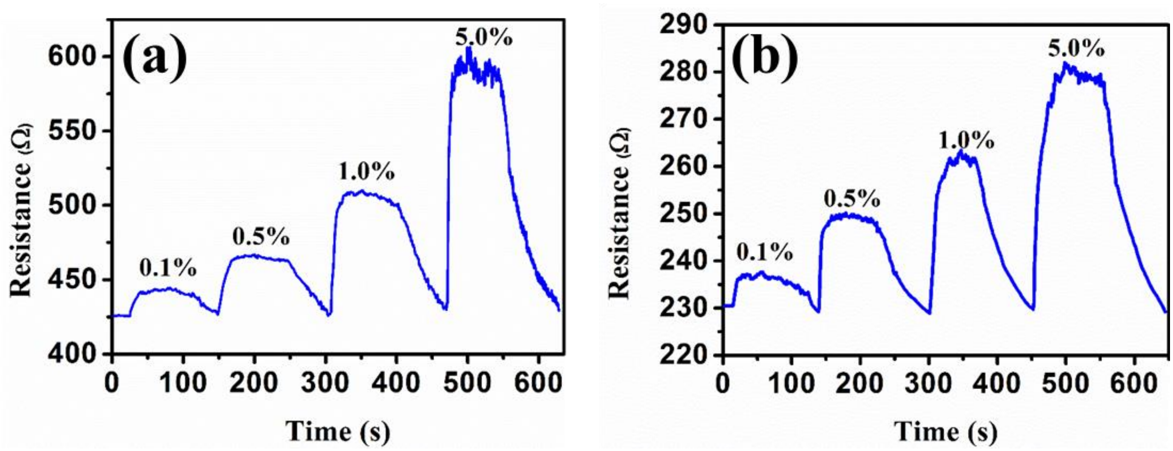

Figure 6.8: Dynamic response resistance upon hydrogen exposure at 150 °C for (a) only MoS_2 film (b) only GaN film.

6.5 SENSING MECHANISM AT MoS2/GaN HETEROINTERFACE

The removing of ambient oxygen and exposing fresh active sites for hydrogen adsorption cannot solely account for very high sensitivity achieved by MoS_2/GaN based heterojunction sensor. Here, we propose another important mechanism- the rising of barrier height at the MoS_2/GaN interface induced by diffusion of hydrogen molecules. The molecules of hydrogen gas are very small as compared to other gases, such as CH_3, CO, CO_2, H_2S. Due to the small size of molecules, hydrogen can easily diffuse at the MoS_2/GaN interface and therefore changes the I-V characteristics at the heterojunction(Alev et al., 2018; Huang et al., 2011). The hydrogen gas diffuses into the MoS_2/GaN interface and perturbs the charge density at the heterojunction. The diffusion phenomenon primarily depends on the temperature, pore radius, and molecular weight of the diffusing gas(Sakai et al., 2001). The diffusion constant is directly proportional to the square root of the temperature. Therefore, increasing the temperature increases the diffusion of hydrogen through MoS_2/GaN interface. Thus, a higher value of sensitivity is obtained with an increase in temperature. However, beyond 150 °C the desorption process prevails over diffusion process leading to decrement in sensitivity. The increase in barrier height upon diffusion of hydrogen molecules significantly reduces the flow of electrons across the MoS_2/GaN heterojunction. This effect strongly influences the reverse bias characteristics as compared to the forward bias characteristics.

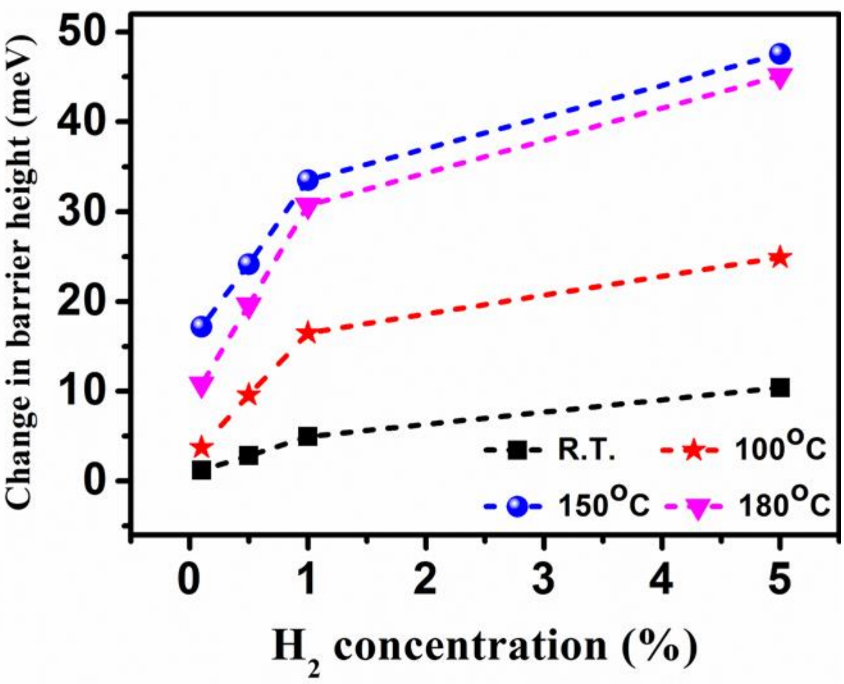

Figure 6.9: Change in barrier height at MoS_2/GaN interface as a function of hydrogen concentration at different values of temperature.

The MoS_2/GaN heterojunction allows modulation of barrier height at the interface upon exposure of hydrogen molecules. The barrier height at the MoS_2-GaN interface can be measured by using the standard thermionic equation(Chen et al., 2011; Crowell and Sze, 1966):

$$I = I_0\left(e^{qV/\eta k_B T} - 1\right) \qquad (6.1)$$

and I_0, the reverse saturation current is expressed as:

$$I_0 = AA^*T^2 e^{-q\Phi_B/k_B T} \qquad (6.2)$$

where η is the ideality factor, k_B is the Boltzmann's constant, T is the operating temperature, A is the contact area, A^* is the effective Richardson's constant (26.4 A cm^{-2} K^{-2} for n-GaN substrate), and φ_B is the barrier height(Kumar et al., 2013). From Eq. 6.1 and 6.2, the barrier height at the MoS_2-GaN interface can be estimated to be 0.872 eV at 150 °C, which increases to a value of 0.905 eV under 1% hydrogen exposure. We have observed the increase in barrier height increases upon hydrogen exposure. Moreover, the change in the barrier height $(\Delta\Phi_B)$ upon exposure to hydrogen gas under reverse bias mode can also be determined by the following relation(Van Vliet, 1995; Wei et al., 2009):

$$\ln(R_0/R_g) = -\Delta\Phi_B/kT \qquad (6.3)$$

The change in barrier height with respect to changes in hydrogen concertation is plotted in Figure 6.9 at four different temperatures for a fixed voltage bias of –3V. Eq. 6.3 demonstrate that due to the exponential dependence of resistance on the barrier height, even a small change in barrier height results in a very large change in resistance, which led to a very high value of sensitivity. We have observed that the change in barrier height upon hydrogen exposure reaches its maximum value at a temperature of 150 °C. The drop in the change in barrier height beyond 150 °C is due to fewer gas molecules interact with the device, and fast desorption prevails over the adsorption process under strong thermal energy.

6.6 CARRIER TRANSPORT ACROSS THE MoS2/GaN HETEROINTERFACE

Figure 6.10(a and b) illustrates the carrier transport process and sensing mechanism of the MoS_2/GaN heterojunction based gas sensor using the energy band diagram. Once the physical contact is formed between MoS_2 and GaN, the smaller work function of GaN allows the electron transfer from the underlying GaN to the stacked MoS_2 film. Subsequently, the downward band-bending near the MoS_2 surface and upward band-bending near the GaN surface will take place to align the Fermi-levels of both the constituent semiconductors. Upon hydrogen exposure, the electron density decreases at the interface as the adsorbed hydrogen molecules take the electrons from MoS_2 film. Thus, the Fermi level of MoS_2 shifts more downward, leading to a further increase in barrier height at the MoS_2/GaN interface. Figure 6.10(b) shows that the barrier height rises by an amount $\Delta\Phi_B$ due to adsorption of hydrogen on the MoS_2/GaN interface. The dotted red line illustrates the raised barrier structure. This rise in barrier height results in a reduction of electrical current across the junction, which led to very high sensitivity. Thus, MoS_2/semiconductor heterojunction based gas sensors exhibit a great potential for tunable sensitivity using reverse bias as a controlling instrument.

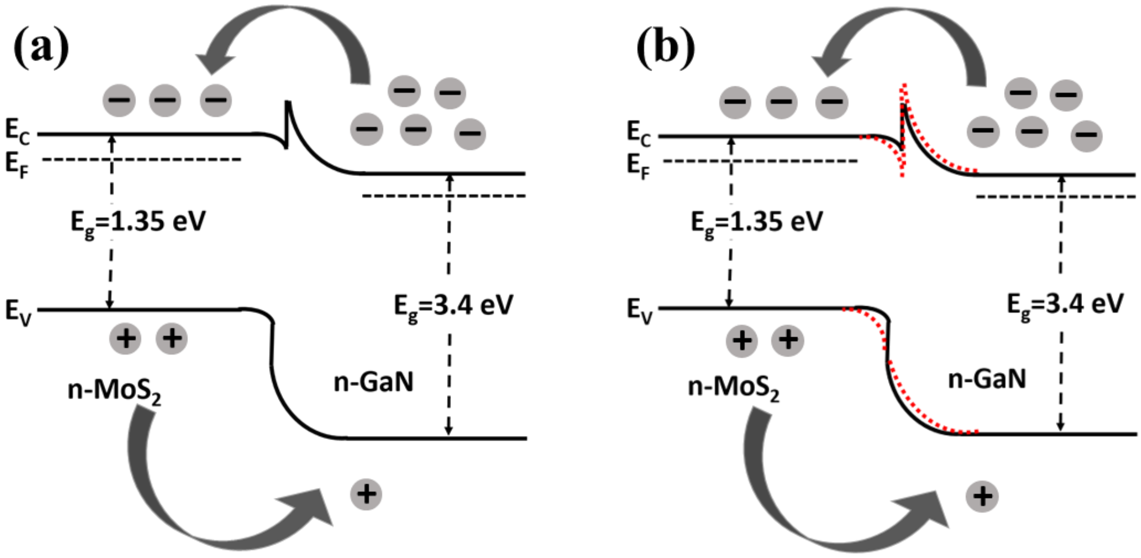

Figure 6.10: The schematic illustration of the energy band diagram of MoS2/GaN heterostructure under reverse bias condition (a) without and (b) with hydrogen exposure. The dotted red line depicts an increase in barrier height in the presence of hydrogen. E_V, E_C, and E_F symbolize the valance band maximum, conduction band minimum, and Fermi level, respectively.

6.7 CHAPTER SUMMARY

In summary, we have successfully fabricated MoS_2/GaN heterojunction based gas sensor using a magnetron sputtering method followed by a sulfurization process. Our method demonstrates a wafer-scaled controlled synthesis of highly crystalline and uniform MoS_2 film. Our proposed sensor showed sensitivity orders of magnitude higher than conventional MoS_2 based sensors. The very high sensitivity of the sensor is due to the modulation of barrier height upon hydrogen exposure under reverse bias operation. This work establishes the MoS_2/GaN heterojunction as a promising candidate for application in highly sensitive gas sensors. Due to the use of GaN as a substrate, our gas sensors can also be integrated with visible blind ultraviolet photodetector applications on the same substrate.

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