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Conclusions, Challenges and Future Work

8.1 CONCLUSIONS

This thesis work presents a systematic study of fabrication and characterization of MoS_2/Si and MoS_2/GaN heterojunctions. We explored their photo- and gas-sensing behaviors of these heterojunctions, which can potentially be used for a variety of applications. In this thesis work, a high-quality MoS_2 film was deposited over various substrates using mechanical exfoliation and magnetron sputtering coupled with sulfurization techniques. Spectroscopic and microscopic characterizations expose the signature of the highly crystalline, homogeneous, and controlled growth of a deposited few-layer MoS_2 film on top of substrates.

The layered TMDs materials grown over the conventional 3D semiconductor substrate ignited a spark of interest in the electronics industry. The integration of 2D layered materials with other materials extensively addressed the formidable challenges faced by the new generation electronic and optoelectronic devices due to their exciting properties. For a deeper understanding of carrier dynamics at the heterointerface, it is necessary to know the band alignment at the heterointerface. Depending on the type of band alignment, the hybrid heterojunctions can be utilized for various potential applications, including optoelectronic devices, quantum well structures, and tunnel diodes.

In the first part of this thesis work, we have visualized the band alignment across the MoS_2/Si and MoS_2/GaN heterojunctions for their different applications. A valence band offset of 0.66 eV and a conduction band offset of 0.42 eV was obtained at the MoS_2/Si interface using X-ray and ultraviolet photoelectron spectroscopy. We determined a type-II band alignment at the MoS_2/Si interface, which is very conducive for the transport of photoexcited carriers. Similarly, a valence band and conduction band offset values of 1.75, and 0.28 eV at the MoS_2/GaN interface was obtained, affirming a type-I band alignment at the heterointerface. Our work paves the way for modeling and designing of different heterojunctions for their distinct applications. Thus, the determination of band offset values and type of band alignment at the 2D/3D heterointerface is essential to pave the way for the integration of TMDs with other 3D materials.

To explore the charge transport in the MoS_2/Si heterojunction, we studied the contribution of different carrier interactions and scattering mechanisms in the conduction process. In this thesis work, we have demonstrated an ultrasensitive photodetector based on MoS_2/Si (for both p- and n-type Si) heterojunction which provides a high photo-responsivity of greater than 10^3 A/W along with a large detectivity of $\approx 10^{12}$ Jones (Jones = cm.Hz$^{1/2}$/W). This high photo-responsivity is attributed to the high absorption rate of incident photons and the large current carrying capacity of few-layer MoS_2. Even a small optical signal can easily be detected due to the high value of responsivity and detectivity. The tuning of barrier height at the MoS_2/n-Si interface with photoexcitation of different wavelengths was interpreted by using Bardeen's model. The increase in carrier density due to photon energy results in a reduction of barrier height at the heterojunction. Because of an increase in carrier density with wavelength, it was observed that the inverse Auger process prevails for the relaxation of photo-induced charge carriers at the MoS_2/Si interface over other scattering mechanisms.

In chapter 6 of this thesis work, we evaluated the UV photo-sensing performance of a 2D/3D heterojunction by depositing MoS_2 on GaN substrate with a mass-scalable sputtering method. The MoS_2/GaN heterojunction exhibit a rectifying behavior with a barrier height of 0.395 eV without illumination. The I-V characteristics measured by varying the light intensity of the incident irradiation from 0 to 70 mW/cm^2 indicate that illumination strongly influences the barrier height at the interface. The FL-MoS_2 is advantageous than its monolayer and multilayer counterpart in terms of its higher light absorption capacity and fast generation and separation of the photo-induced charge carriers. Our device shows a high external spectral responsivity (~10^3 A/W) and detectivity (~10^{11} Jones) with very fast response time (~5 ms). This work unveils a new perspective of MoS_2/GaN heterojunction for high-performance optoelectronic applications.

In the last part of this thesis work, we evaluated the sensing performance of MoS_2/GaN heterojunction. Our proposed sensor showed sensitivity orders of magnitude higher than conventional MoS_2 based sensors. Due to the oxidizing nature of hydrogen, it takes electrons from MoS_2/GaN heterojunction and changes the carrier concentration through charge transfer. Due to decrement in carrier density after hydrogen adsorption, the resistance of the device increases sharply, resulting in a change in the obtained electrical signal. Moreover, hydrogen has a smaller molecular size as compared to other gases; hence, it can diffuse more at the MoS_2/GaN interface and increases the device resistance rapidly. The diffusion of a gas strongly depends upon temperature, and it increases with an increase in temperature. Thus, to increase the sensitivity of our sensor, we increase the temperature of our device. We observed that a very high value of sensitivity could be obtained at 150 °C. However, increasing the temperature beyond 150 °C leads to a decrement in sensitivity. This decrement is due to the dominance of desorption process over adsorption process at a very high temperature.

The diffusion of hydrogen is not sufficient to explain a very high value of sensitivity. Interestingly, we propose another very important mechanism that plays a crucial role. The rising of barrier height at the MoS_2/GaN junction due to diffusion of hydrogen molecules is the main driving force for the very high sensitivity of the sensor. The resistance depends exponentially on barrier height; therefore, even a small change in barrier height leads to an enormous change in resistance, resulting in a very high value of sensitivity. Furthermore, our hydrogen sensor consumes power in µW as compared to conventional hydrogen sensors, which consume power in mW. This ultralow power consumption (1000 times lesser than conventional hydrogen sensors) is due to the reverse bias operation of our gas sensor. 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.

Therefore, the potential application of 2D/3D hybrid heterostructures opens up new possibilities to develop new advanced hybrid materials for various fields, such as in nanoelectronics and optoelectronics devices. The unique, exciting physics of 2D material and their heterostructures assist in discovering new designs and functionalities of the electronic devices, including photo and gas-sensors. The reverse bias operation of the devices results in ultralow power consumption, while a drastic change in reverse current with a slight change in barrier height due to its exponential dependence leads to a very high value of sensitivity. The properties of the heterostructures can easily be tailored according to a specific requirement just by changing the thickness of the constituent materials or by the doping process.

8.2 CHALLENGES AND FUTURE WORK

According to the WHO global air quality database 2018, more than 91% of the world population is exposed to air quality levels that exceed the safe permissible limits. This alarming air pollution causes heart diseases, lung diseases, and several other non-communicable diseases that claim around 7 million lives per year. Thus detection of gases causing air pollution is an absolute necessity to take preventive measures. The 2D materials establish themselves as promising gas-sensing materials due to their large surface-to-volume ratio and very simple sensing mechanism based on a change in resistance of the material.

The development of efficient and reliable sensing systems has attracted intense research interest in detecting gas molecules at a low concentration. However, the current technologies face several impediments restricting their performance in gas sensing applications. Most of the gas sensor in the realm of gas sensing technology has been developed by metal oxide semiconductors such as ZnO, SnO_2, TiO_2, and WO_3, in different forms. However, conventional metal oxide-based gas sensors operate at elevated temperatures (> 200°C)(Ou et al., 2015). Extra heating elements with metal oxide sensing layers make it bulky and complex devices with large power consumption. Besides these drawbacks, selectivity is also one of the most critical issues to detect a low concentration of targeted gas molecules in the presence of other interfering gases. The other approaches, including using organic semiconductors for making efficient gas sensors also suffer setbacks due to the low value of mobility of charge carriers and high operating voltages(Gao, 2017).

Newly explored 2D materials have an extra edge over conventional technologies, particularly for sensing applications due to their atomic thickness, inherently high surface to volume ratio, tunable bandgaps, high surface sensitivity, a large value of carrier mobility, and abundant adsorption sites on their surfaces. Graphene has already registered its strong presence in the field of gas sensing by detecting a single molecule adsorbed on its surface because of its exceptionally low-noise level. These promising sensing results had never been achieved by using any other existing technology. Although some of the 2D materials can sense at room temperature, however, due to slow kinetics at room temperature, they suffer from the slow response and recovery times of the sensor(Kim et al., 2019).

Recently, mixed dimensional semiconductor heterostructures (0D/2D, 1D/2D, and 2D/3D) have been recognized as an essential building block to create a solid-state device. These heterostructures depict very high sensitivity and extremely low power consumption when operated under reverse bias conditions as compared to their mono-dimensional counterparts. These heterostructures offer a barrier for the movement of charge carriers at the heterointerfaces. The modulation of barrier height at the heterointerface due to diffusion of gas molecules is the main driving force for the very high sensitivity of these sensors(Goel et al., 2019). The resistance depends exponentially on barrier height; therefore, even a small change in barrier height leads to an enormous change in resistance, resulting in a very high value of sensitivity. However, most of the heterostructures based gas sensor also suffers from the same high operating temperature and selectivity problems to detect a low concentration of targeted gas molecules.

8.2.1 The specific objectives of the future work

In our future endeavors, we will grow mixed dimensional heterostructures for gas sensing applications without any micro-heater and which would operate at room temperature. The following will be the main objectives of our future endeavors.

- Growth of different dimensional materials on various substrate
- Synthesis of mixed dimensional heterostructures particularly those combinations having at least one 2D component, for instance, 0D/2D, 1D/2D, 2D/2D, and 2D/3D
- Microscopic and spectroscopic characterization of the grown heterostructures
- Investigating the gas sensing behavior of synthesized heterostructures against various environmental pollutants (selectivity) with consuming power in μW range

- Evaluate the reversibility and stability characteristics of the sensors in the air atmosphere at room temperature

- Exploring the interfacial dynamics at different heterojunctions to understand the carrier transport process at the heterointerfaces

8.2.2 Suggested action plan to achieve the future objectives

In the realm of gas sensor technology, our future work is an attempt to develop highly selective gas sensors at room temperature with an interdisciplinary effort.

- Scalable growth of 2D based heterostructures remains a major bottleneck preventing their uses for commercial applications. The most widely used conventional mechanical exfoliation and chemical vapor deposition techniques have their own limitations. Therefore, we can use some modified approaches for the scalable fabrication of these heterostructures.

- Another difficulty in making mixed dimensional heterostructures is making reliable contacts to an individual material. Contact engineering is required at the metal-semiconductor interface to make efficient charge transport across the heterointerfaces. By using some solvent-based techniques or dry chemical processes, we can achieve the optimal contacts for enhancing the overall performance of the sensors.

- We can use optical energy (for example, UV lamps) in place of thermal energy, as the former results in a fast response and complete recovery at room temperature due to in situ cleaning and charge perturbation on the sensing surface. Optical illumination also decreases the power consumption of the device from mW to µW level.

- High selectivity of the gas sensors can be achieved through the functionalization of the sensing layer by employing noble metal nanoparticles. Moreover, metal nanoparticles decrease the detection limit due to metal's catalytic effect and more number of active sites through surface modifications.

- The interfacial physics, specifically for 2D based heterojunctions, is still elusive. For instance, the formation of the depletion layer between atomically thin materials requires further study as the order of depletion width may be much higher than the physical thickness of these materials. Therefore, in our future endeavors, we will explore the interfacial dynamics at different heterojunctions to understand the carrier density distribution and the transport processes.

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