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Conclusions, and Scope for Future Work

This chapter summarizes the key challenges addressed and accomplishments achieved during this thesis work, aligning with the objectives outlined in Chapter 1. Significant progress was made in overcoming challenges related to the growth and application of 2D layered materials, MoS_2 and SnS_2, for gas sensing and photodetector devices. By optimizing the chemical vapor deposition (CVD) process, large-area, uniform flakes of MoS_2 and SnS_2 were successfully synthesized on SiO_2/Si substrates, resolving issues of uniformity and reproducibility. Advanced NO_2 gas sensors were developed using nitrogen plasma-treated MoS_2 with Ag nanoparticle functionalization and vacancy-assisted, vertically aligned SnS_2 structures, achieving selective, sensitive, and recoverable NO_2 detection. Additionally, photodetectors based on MoS_2-WS_2 heterostructures were fabricated, demonstrating enhanced optical absorption and responsivity compared to pristine MoS_2 devices. These advancements addressed critical challenges such as low optical absorption and large transient response times, paving the way for high-performance broadband photodetectors and sensitive gas sensors.

8.1 Conclusions

This thesis work addresses several important concerns and challenges pertaining to gas sensing and photodetectors. The following is a summary of all the results of this thesis work:

Our study underscores noteworthy progressions within the domain of gas sensing, particularly concerning the sensing of NO_2, leveraging two-dimensional materials such as MoS_2 and SnS_2. An extensive investigation was undertaken regarding the wafer-scale fabrication of MoS_2 and SnS_2 flakes exhibiting precisely controlled morphologies, facilitating a transition from in-plane to vertically oriented configurations, achieved by optimizing pivotal growth parameters including gas flow rate and temperature throughout the thermal chemical vapor deposition (CVD) methodology. The pivotal role of gas flow rate in shaping the morphology and orientation of the flakes was accentuated. Comprehensive morphological, structural, optical, and spectroscopic evaluations were executed utilizing techniques such as SEM, FESEM, XRD, Raman, PL, and XPS to elucidate the electrical and optical characteristics of the synthesized films. These characterizations validated the exceptional uniformity, reproducibility, and wafer-scale coverage of the synthesized MoS_2 and SnS_2 flakes on SiO_2/Si substrates. A growth mechanism was proposed to elucidate the kinetic processes involved in the transition from 2D in-plane to 3D vertically aligned structures. Interdigitated electrode (IDE) patterns were employed to facilitate electrical measurements of the devices, leveraging the tailored properties of MoS_2 and SnS_2.

Moreover, this investigation delved into the formulation of diverse MoS_2 and SnS_2 based NO_2 gas sensor with enhanced performance. The gas sensing experiments demonstrated that SnS_2 serves as a highly suitable candidate for NO_2 gas sensors as compared to MoS_2. The sensitivity of these sensors was further enhanced through generation of defect and doing using nitrogen plasma treatment, and surface engineering using noble metal nanoparticle like Ag, whereby alterations in morphology and structure generated varying quantities of reactive sites for interactions with gas molecules. Additionally, the application of CVD-grown MoS_2 in optoelectronics was scrutinized through the fabrication of WS_2/MoS_2 heterojunction photodetectors capable of functioning across the visible to near-infrared light spectrum. These advancements provide significant insights and practical contributions towards the evolution of high-performance gas sensors and photodetectors for commercial applications.

Research on MoS_2 gas sensing generally demonstrated excellent gas sensing performance by interface and defect engineering independently, but no investigation on a thorough

combined effect of both was provided. This is the cause; we demonstrate that the sensing performance of CVD grown MoS_2-based NO_2 gas sensors can be significantly improved through the nitrogen doped and defect-selective surface functionalization of Ag NPs. Utilizing a combination of Raman spectroscopy and X-ray photoelectron spectroscopy, we validated the effective p-doping of MoS_2 through nitrogen plasma treatment and established beneficial band alignment, which is integral to the dynamics of charge carriers. Our comparative evaluation of the sensing responses from pristine MoS_2, N-MoS_2, Ag-MoS_2, and Ag-N-MoS_2 devices at an elevated temperature of 100 °C reveals that the Ag-N-MoS_2 configuration displays the most pronounced sensitivity to NO_2, thereby highlighting the synergistic interactions between silver nanoparticles and nitrogen doping. The Ag-N-MoS_2 sensor exhibited a remarkable response to NO_2 achieving 71.02% at 50 ppm at at 100 °C, with fast response (27.17 s) and recovery times (132.24 s). These results imply that Ag-N-MoS_2 possesses significant promise for the development of highly sensitive and efficient gas sensors.

Moreover, the response of the NO_2 gas sensor based on MoS_2, even after nitrogen plasma treatment to introduce doping and defects, as well as surface functionalization with Ag nanoparticles, is relatively lower compared to other 2D materials due to its inherently lower adsorption energy towards NO_2 molecules. Hence. we have successfully synthesized a highly sensitive gas sensor predicated upon vertically aligned SnS_2 flakes through the application of the chemical vapor deposition (CVD) methodology, thereby demonstrating remarkable selectivity towards NO_2 in comparison to over a range of other toxic and combustible gases. The fabricated SnS_2 sensors exhibited commendable stability in performance, elevated sensitivity (164%), and expeditious response/recovery times (41/309 s), when exposed to 50 ppm NO_2 at 120 °C. Moreover, we investigated the fast nitrogen plasma treatment technique as a means to engender sulfur vacancies on the SnS_2 surface, thereby significantly augmenting its functionalization and gas sensing attributes. The sensors subjected to 12 minutes of nitrogen plasma treatment exhibited an extraordinary response of 246% to 50 ppm NO_2, signifying an approximate 1.5 order-of-magnitude enhancement relative to pristine SnS_2. The pronounced selectivity of the sensor towards NO_2, even amidst the presence of assorted interfering gases such as CH_4, CO, H_2, H_2S, CO_2, and NH_3, accentuates its promising applicability for low-concentration gas detection in domains such as medical diagnostics, industrial processing, and environmental monitoring.

In addition, Density functional theory (DFT) calculations were conducted to evaluate the NO_2 gas adsorption properties on three functionalized MoS_2 monolayers: pristine MoS_2, nitrogen-doped MoS_2 (N-MoS_2), and silver-functionalized nitrogen-doped MoS_2 (Ag-N-MoS_2). For pristine MoS_2, weak van der Waals interactions were observed between the surface and NO_2 molecules, with the lowest adsorption energy of -0.53 eV. Nitrogen doping enhanced the adsorption energy to -0.75 eV, with noticeable symmetry breaking in the NO_2 molecule due to unequal bond lengths and a dominant non-bonding interaction between oxygen and nitrogen on the surface ($d_{O\text{-}N(surface)}$ = 2.06 Å). Further functionalization with silver nanoparticles significantly increased the adsorption energy to -1.33 eV. Additionally, SnS_2 monolayers demonstrated a higher NO_2 binding affinity compared to other gases, with an adsorption energy of -1.91 eV, attributed to an increase in carrier concentration upon NO_2 adsorption. DFT studies also revealed that sulfur-vacancy defects on SnS_2 surfaces shifted the adsorption mechanism from physisorption to chemisorption. Among three optimized structures, the highest adsorption energy (2.19 eV) was observed for the structure with one sulfur vacancy, outperforming pristine SnS_2. Using the Lee and Strano reaction mechanism to model gas sensing, it was found that the N12 sample exhibited a higher forward rate constant ($k_{ir(ads)}$ =1.39 x 10^{-4} $(ppm.s)^{-1}$) than NO sample $k_{ir(ads)}$ =1.56 x 10^{-5} $(ppm.s)^{-1}$) at an operating temperature of 120°C, highlighting the enhanced sensing performance of functionalized materials.

We also demonstrated a self-powered photodetectors based on the MoS_2-WS_2 heterostructure were successfully fabricated by decorating WS_2 onto MoS_2 films grown using chemical vapour deposition (CVD) techniques. The surface morphology and structural

features of the MoS_2-WS_2 heterojunctions were assessed using several analytical techniques, including XPS, Raman spectroscopy, FESEM and photoluminescence spectroscopy. By leveraging the effective interlayer charge transfer mechanism between WS_2 and MoS_2, the MoS_2-WS_2 device demonstrates a notable photoresponsivity of 282.77 mA/W and a specific detectivity of 6.44 x 10^{12} Jones. Additionally, the device exhibits a response time of ~375µs/6ms, which represents a significant improvement in photoresponsivity compared to the pristine MoS_2 and WS_2 devices. Moreover, anchored WS_2 with MoS_2 may pave the way towards the development of high-performance practical optoelectronic devices due to exceptional stability, high response and dependability in response to visible-NIR radiation in the air.

8.2 Scope for Future Work

The present thesis has made significant contributions to the field of 2D materials, particularly in the development of MoS_2 and SnS_2 for applications in gas sensing and photodetection. However, there remain exciting opportunities to further advance this research. One promising direction is the adoption of transfer techniques to create heterojunctions on large-area MoS_2 and SnS_2, which could significantly enhance the performance and functionality of these materials by enabling the integration of diverse components. Additionally, the fabrication of flexible and wearable devices is increasingly important due to their potential applications in healthcare and consumer electronics. This requires innovative fabrication techniques and the use of flexible materials, leading to the development of versatile devices that can be seamlessly integrated into daily life.

Moreover, the creation of photodetectors and gas sensors capable of operating under extreme conditions presents a significant opportunity for various industries. For instance, high-temperature photodetectors could be utilized in industrial processes, while gas sensors designed to function in high humidity environments would be valuable in agriculture and environmental monitoring. The current experimental findings have established a foundation for these advancements, but further exploration is needed in several areas.

The CVD growth of MoS_2 and SnS_2 flakes still offers room for discovering new morphologies that could enhance their electrical and optical properties across different dimensions (zero, one, and three-dimensional). Understanding the growth mechanisms behind these morphologies is essential, as combining different dimensionalities could lead to improved optical and electronic characteristics. Additionally, while the response and recovery times of gas sensors are critical, achieving rapid response times in the milliseconds or microseconds range remains a challenge. The influence of morphology on gas diffusion within the sensing film warrants further investigation, as the position of gas molecule adsorption on MoS_2 and SnS_2 significantly affects sensor performance. Enhancing the number of adsorption sites for NO_2 could not only improve sensor response but also increase selectivity.

Despite the advancements in optical absorption through heterojunction formation, the low optical absorption of bare MoS_2 and SnS_2 remains a challenge. This issue could be addressed by synthesizing various morphologies of these materials, such as transitioning from in-plane to vertically aligned structures, which would enhance optical absorption. Investigating the role of plasmonic nanoparticles embedded between vertically aligned MoS_2 and SnS_2 flakes could further improve light absorption for broadband photodetectors. Additionally, the impact of metal nanoparticles on different morphologies of MoS_2 and SnS_2 should be explored to enhance and selectively target NO_2 gas sensing.

Overall, while the ongoing efforts in developing MoS_2 and SnS_2 gas sensors have yielded promising results, there is still a need to optimize their morphologies, structures, and hybrid configurations for practical applications. A more detailed understanding of the gas sensing mechanisms, considering factors such as surface states, edge sites, defects, crystallinity, and electronic properties, is essential. Quantitative calculations of adsorption energy and the number of adsorption sites are crucial for elucidating the gas-sensitive properties of these

materials. The exploration of van der Waals heterostructures involving MoS_2 and SnS_2 is still in its infancy, presenting exciting opportunities for researchers to advance this field toward commercial applications.

Furthermore, the integration of 2D materials like MoS_2 and SnS_2 into flexible and stretchable devices is a burgeoning area of research. Their low power consumption, high charge carrier mobility, lightweight nature, and excellent mechanical properties make them ideal candidates for applications in flexible gas sensors and broadband photodetectors. The potential for these materials to be used in wearable technology is vast, particularly for real-time environmental monitoring and healthcare applications. The replacement of rigid metal electrodes with flexible 2D metallic materials in sensor devices could enhance performance, transmittance, and flexibility, paving the way for e-skin and e-textile nano-gas sensors that improve conformal contact with the human body.