Preface

Molybdenum disulfide (MoS_2) is one of the widely explored representative members of the transition metal dichalcogenide family, attributed to its notable semiconducting characteristics, atomic-scale thickness, robust spin–orbit coupling, tunable bandgap, and advantageous optoelectronic properties. This thesis entitled "**Layer, Morphology and Substrate Dependent Anisotropic, Thermal and SERS Studies of CVD Grown 2H-MoS_2"** is focused on the semiconducting, anisotropic and thermal conducting MoS_2 nanostructures of different layer number and different morphologies grown over different substrates, synthesized via chemical vapor deposition (CVD) technique and is utilized for Surface-Enhanced Raman Scattering (SERS) applications. We have prepared five different types of MoS_2 nanostructures- horizontally grown triangular (1L, 3L and 5L, where L is the layer number) MoS_2 over SiO_2-Si substrate (1L, 3L and 5L MoS_2/SiO_2-Si), horizontally grown thin film MoS_2 over SiO_2-Si substrate (H-MoS_2/SiO_2-Si), vertically oriented few-layer MoS_2 over SiO_2-Si substrate (V-MoS_2/SiO_2-Si), horizontally grown thin film MoS_2 over FTO coated glass substrate (H-MoS_2/FTO) and vertically oriented few-layer MoS_2 over Si substrate (V-MoS_2/Si). The morphologies of these as-synthesized films were observed by optical microscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), Raman, photoluminescence (PL) and UV-visible spectrophotometer. The phase and the semiconducting feature were confirmed via Raman and photoluminescence (PL) spectra. Further, to confirm the layer number, these films were characterized via atomic force microscopy (AFM) techniques.

Firstly, we elucidated the tunability of the bandgap for different layered MoS_2 nanostructures by analyzing the contribution of spin orbit coupling (SOC) and interlayer coupling (ILC) observed both theoretically (electronic band structure via first-principles density functional theory) and experimentally (Raman and PL spectroscopy). Also, we demonstrate the thermally driven bandgap tunability in low-temperature regime (80-300 K) for different layered (1, 3 and 5L) triangular MoS_2, H-MoS_2/SiO_2-Si, V-MoS_2/SiO_2-Si and H-MoS_2/FTO, showing new functionalities in optoelectronics and photonics applications that demands external modulation of optical properties. Next, we observed the theoretical origin of possible phonon modes in different layered (1 to 6L) MoS_2 nanostructures using group theory and density functional perturbation theory (DFPT). The phonon dispersion curve along with their phonon density of states (DOS) for 1 to 6L MoS_2 shows the evolution of phonon modes with increasing layer number and contribution of each atom to the total phonon DOS, respectively. Further, we studied the systematic optical anisotropic study to observe the electron-phonon-photon coupling effect in different layered (1, 3 and 5L) triangular MoS_2, using angle resolved polarized Raman spectroscopy (ARPRS) study under non-resonant (532 nm) and resonant (633 nm) excitation wavelengths. An unexpected behavior in polarized Raman study of E^1_{2g} phonon mode is observed under 633 nm excitation, in contrast to 532 nm excitation wavelength and has been discussed by incorporating Frohlich exciton-phonon interaction. Similar study was conducted to illustrate the effect of orientation (horizontal and vertical) of MoS_2 nanostructure on anisotropic response. The different anisotropic response of V-MoS_2/SiO_2-Si compared to horizontally oriented film of MoS_2 is observed due to the symmetry breaking of the vertical nanosheets, oriented at different angles with the substrate. We also performed the ARPRS study on large area thin film of horizontally oriented MoS_2 grown over conducting substrate, i.e. on H-MoS_2/FTO, exhibiting similar behavior like H-MoS_2/SiO_2-Si. The optical anisotropic response of these materials promises the wide-open field prospective applications in MoS_2-based photonic and optoelectronic devices like polarization-sensitive photodetectors, phototransistors, linearly polarized pulses generators, optical waveplates, optical switches and interconnects, etc.

Further, we studied the thermal transport behavior of different layered (1, 3 and 5L) triangular MoS_2, H-MoS_2/SiO_2-Si, V-MoS_2/SiO_2-Si and H-MoS_2/FTO, and quantitatively analyzed the non-linear temperature-dependent Raman shift in low-temperature regime (80-300 K) by using a physical model that includes thermal expansion, three- and four-phonon anharmonic effects. It is observed that the nonlinear thermal transport response of E^1_{2g} and A_{1g} phonon modes in prepared MoS_2 films primarily originates from three-phonon process and a weak contribution from the four-phonon process, because the four-phonon process involves large number of phonons and so is less likely to occur than the three-phonon process. We also measured the interfacial thermal conductance (g) and thermal conductivity (k_s) of the synthesized films using optothermal Raman spectroscopy technique. Thermal conductivity measurements of horizontally oriented triangular MoS_2 films suggests decreasing thermal conductivity with increasing number of layers. The comparative analysis of orientation dependent thermal transport behavior of CVD grown MoS_2 over SiO_2-Si substrate shows the larger contribution of higher order (four) phonon scattering for in-plane vibrational mode in H-MoS_2 due to large area interface formation between H-MoS_2 and SiO_2-Si substrate compared to V-MoS_2. This leads to higher interfacial thermal conductance and lower thermal conductivity of H-MoS_2/SiO_2-Si compared to V-MoS_2/SiO_2-Si. The lesser interface formation between V-MoS_2 and SiO_2-Si substrate leads to minimal strain in V-MoS_2 giving it a suspended like characteristics and hence result in higher in-plane thermal conductivity. The H-MoS_2/FTO shows higher g and k_s values compared to H-MoS_2/SiO_2-Si due to the better thermal transport property of FTO substrate compared to SiO_2-Si substrate. These studies clearly suggest that good thermal conductivity of prepared MoS_2 films, make them suitable for thermal management in MoS_2 based electronic and optoelectronic devices.

Based on the semiconducting nature of the different prepared MoS_2 nanostructures, we have utilized these films for SERS applications. We have successfully detected two important biomolecules: bilirubin and vitamin B_{12} (Cyanocobalamin), using H-MoS_2/FTO, V-MoS_2/Si, V-MoS_2/SiO_2-Si and H-MoS_2/SiO_2-Si SERS substrates. The highest detection limit of 10^{-11}

and 10^{-8} M were obtained for bilirubin and vitamin B_{12}, respectively on the prepared H-MoS_2/FTO and V-MoS_2/Si SERS substrates. Also, we have demonstrated the low temperature enhanced SERS activity on CVD grown pristine MoS_2 films over different substrates.

The present thesis has been organized into seven chapters as following-

Chapter 1 gives detailed introduction of 2D MoS_2 nanostructure and the literature review on semiconducting response, optical anisotropy, thermal conductivity and SERS application of 2D MoS_2.

Chapter 2 describes the synthesis process of five different MoS_2 nanostructures with different layer number and morphology, grown over different substrates. A characterization concise overview of the instruments is provided for structure and morphology of MoS_2 through optical microscopy, SEM, AFM, Raman, PL and UV-Visible.

Chapter 3 discusses the tunability of the bandgap for different layered MoS_2 nanostructures observed both theoretically (electronic band structure via first-principles density functional theory) and experimentally (Raman and PL spectroscopy). Also, we demonstrate the thermally driven bandgap tunability in low-temperature regime for different layered (1, 3 and 5L) triangular MoS_2, H-MoS_2/SiO_2-Si, V-MoS_2/SiO_2-Si and H-MoS_2/FTO.

Chapter 4 discusses the theoretical origin of possible phonon modes in different layered (1-6L) MoS_2 nanostructures using group theory and density functional perturbation theory (DFPT). We also examine the optical anisotropic response of prepared MoS_2 films to observe the electron-phonon-photon coupling effect and its dependence on layer number, excitation wavelengths (non-resonant and resonant) and orientation of the film with substrate, using angle resolved polarized Raman spectroscopy (ARPRS).

Chapter 5 discusses the thermal transport behavior that includes thermal expansion, three- and four-phonon anharmonic effects and calculated the interfacial thermal conductance and thermal conductivity of different layered (1, 3 and 5L) triangular MoS_2, H-MoS_2/SiO_2-Si, V-MoS_2/SiO_2-Si and H-MoS_2/FTO.

Chapter 6 discusses the SERS detection of bilirubin and vitamin B_{12} (cyanocobalamin) using different prepared MoS_2 nanostructures. Also, we have discussed the vibronic coupling enable charge transfer mechanism with experimental verification of quenching of PL peak and have calculated the enhancement factor. Also, low temperature enhanced SERS activity on different prepared substrates were performed.

Chapter 7 summarizes the thesis work and the scope for future work related to this field has been discussed.