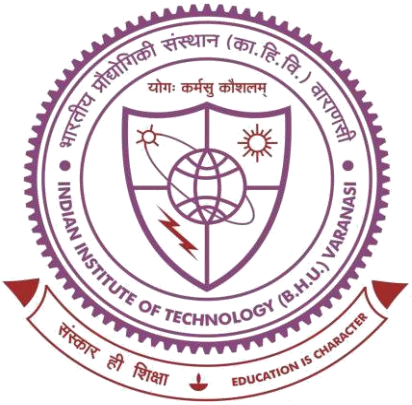
Layer, Morphology and Substrate Dependent Anisotropic, Thermal and SERS Studies of CVD Grown 2H-MoS_2



Thesis submitted in partial fulfilment

for the Award of

Doctor of Philosophy

By

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Chapter 7 Conclusion and Future Scope of The Work

7.1 Conclusion

In conclusion, thesis work is mainly focused on the synthesis of semiconducting, anisotropic and thermal conducting two-dimensional MoS_2 nanostructures via chemical vapor deposition (CVD) technique and investigation for Surface-Enhanced Raman Scattering (SERS) application. We have synthesized five different morphologies of MoS_2 nanostructures with different orientation (horizontally/vertically) grown over different substrates [SiO_2-Si, fluorine-doped tin oxide (FTO) coated glass and Si]. The morphologies of the prepared nanostructures have been characterized using optical microscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques. The phase and the semiconducting nature of the prepared nanostructures have been confirmed via Raman and Photoluminescence (PL) studies.

Firstly, we have 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). We also 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 have observed the theoretical origin of possible phonon modes in different layered (1-6L) 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 1-6L MoS_2 shows the evolution of phonon modes with increasing layer number and contribution of each atom to the total phonon DOS. Further,

we have studied the systematic optical anisotropic study to observe the electron-phonon-photon coupling effect in 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, using angle resolved polarized Raman spectroscopy (ARPRS) study under non-resonant (532 nm) and resonant (633 nm) excitation wavelengths. 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 examine 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). We have also measured the interfacial thermal conductance (g) and thermal conductivity (k_s) of the synthesized films using optothermal Raman spectroscopy technique, suggesting suitability of thermal dissipation 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. We have also demonstrated the low temperature enhanced SERS activity on CVD grown pristine MoS_2 films over different substrates.

Important Finding of The Present Work

- We have elucidated the electronic band structure and total DOS of 1 to 6L MoS_2 using DFT calculation. Monolayer MoS_2 shows a direct bandgap of 1.74 eV, which decreases with increasing layer number due to fierce competition between SOC and ILC effect, transforming it to indirect bandgap beyond monolayer.

- We studied the temperature-dependent PL spectra of prepared MoS_2 films showing quenching of the PL peak (A-exciton) intensity, broadening of FWHM and red shift of the PL peak position with increasing temperature. The increase in the strength of electron-phonon coupling (S) and average phonon energy $\langle \hbar\omega \rangle$ with increasing layer number, clearly indicates the enhanced electron-phonon interaction with increasing layer number.

- We have comprehensively studied the anisotropic responses of CVD grown triangular MoS_2 with different layer numbers and excitation sources (resonant and non-resonant). 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.

- We illustrated the effect of orientation (horizontally and vertically grown) 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 have quantitatively analyzed the non-linearity in the temperature-dependent Raman response of CVD grown different layered (1L, 3L and 5L) triangular MoS_2/SiO_2-Si using a physical model that includes thermal expansion, three- and four-phonon anharmonic effects. It is observed that the three-phonon scattering rules over the four-phonon scattering and thermal expansion contribution for both the Raman modes. We also observed that both three- and four-phonon scattering decreases as the number of layer increases. Further, we measured the interfacial thermal conductance (g) and thermal conductivity (k_s). The obtained values of g are 0.97 ± 0.20, 4.04 ± 0.01 and 6.08 ± 0.17 MW m^{-2} K^{-2}, and the obtained values of k_s are 50 ± 2, 34 ± 2 and 28 ± 2 W m^{-1} K^{-1} for 1L, 3L and 5L supported MoS_2, respectively.

- We conducted a comparative analysis of orientation dependent thermal transport behavior of CVD grown MoS_2 over SiO_2-Si substrate. The contribution of higher order (four) phonon scattering for in-plane vibrational mode is larger in H-MoS_2 compared to V-MoS_2 due to large area interface formation between H-MoS_2 and SiO_2-Si substrate, leading to higher g in H-MoS_2/SiO_2-Si (~5.89 ± 0.40 $MWm^{-2}K^{-1}$) compared to V-MoS_2/SiO_2-Si (~0.77 ± 0.01 $MWm^{-2}K^{-1}$). 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 for V-MoS_2 (~62 ± 2 $Wm^{-1}K^{-1}$) compared to H-MoS_2 (~33 ± 3 $Wm^{-1}K^{-1}$).
- We also studied the phonon anharmonicity and thermal conductivity of CVD grown MoS_2 film over conducting FTO coated glass substrate. The H-MoS_2/FTO shows higher values of thermal conductivity (k_s ~40 ± 2 $Wm^{-1}K^{-1}$) and interfacial thermal conductance (g ~7.22 ± 0.02 $MWm^{-2}K^{-1}$) compared to H-MoS_2/SiO_2-Si due to the better thermal transport property of FTO in comparison to SiO_2-Si substrate.
- The highest detection limit of 10^{-11} and 10^{-8} M were obtained for bilirubin and vitamin B_{12}, respectively on prepared H-MoS_2/FTO and V-MoS_2/Si SERS substrates. The high SERS performance of H-MoS_2/FTO is attributed to its porous nature and n-type doping due to FTO substrate. While the high SERS performance of V-MoS_2/Si is contributed by the vertical morphology, leading to enhanced light trapping via multiple reflections and better adsorption of molecules within free standing MoS_2 nanosheets.

7.2 Future Scope of the Work

- In the future, the exploration of CVD synthesis techniques could be pursued for synthesizing various 2D transition metal dichalcogenide (TMD) materials and their Janus structures, such as MoSSe, or heterostructures like MoS_2/WS_2, MoS_2/$MoSe_2$, etc.

- Exploration of semiconducting, anisotropic and thermal transport properties of these Janus structures and heterostructures would present an intriguing avenue for research.
- These Janus structures or heterostructures can be explored for SERS applications.
- In the future, there is potential for transferring MoS_2 nanostructures and TMDs heterostructures onto flexible substrates, enabling their utilization in flexible optoelectronic devices.