Dedicated to my Beloved Grandparents and Family

CERTIFICATE

It is certified that the work contained in the thesis titled ***"CVD GROWN THERMAL CONDUCTING 2D-MoS_2 NANOSTRUCTURES FOR PHOTODETECTION AND SERS APPLICATIONS"*** by **"*BISHNU PADA MAJEE*"** has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

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DECLARATION BY THE CANDIDATE

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This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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Date:

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Table of Contents

List of Figures

List of Tables

List of Abbreviations

AEF	Analytical enhancement factor
AFM	Atomic force microscopy
CM	Chemical enhancement
CVD	Chemical vapor deposition
CBM	Conduction band minima
CuPc	Copper phthalocyanine
CV	Crystal Violet
DI	Distilled water
EM	Electromagnetic enhancement
eV	Electron volt
LWD	Long working distance
MW	Mega watt
MB	Methylene blue
MO	Methyl orange
MEMS	Microelectrochemical system
MoS_2	Molybdenum disulphide
NA	Numerical aperture
1D	One dimensional
OTR	Optothermal Raman
ppm	Parts per million
PL	Photoluminescence
PVD	Physical vapor deposition
R6G	Rhodamine 6G

RT	Room temperature
SEM	Scanning electron microscope
SThM	Scanning thermal microscope
SAED	Selected area electron diffraction
Si	Silicon
SiO_2	Silicon dioxide
Ag	Silver
SERS	Surface enhanced Raman spectroscopy
SPR	Surface plasmon resonance
TEC	Thermal expansion coefficient
TDTR	Time domain thermo reflectance
TEM	Transmission electron microscopy
TMD	Transition metal dichalcogenide
2D	Two dimensional
UV	Ultraviolet
VBM	Valence band maxima
VFL	Vertically oriented few-layer
Vis	Visible
XRD	X-ray diffraction

List of Symbols

$\boldsymbol{\alpha}$	Absorption coefficient
ω	Angular frequency
E_g	Bandgap
$\mathbf{k_b}$	Boltzmann's constant
E_c	Conduction band
I-V	Current voltage
ρ	Density of material
q	Electronic charge
E_F	Fermi energy
$\boldsymbol{\chi_P}$	First order power coefficient
$\boldsymbol{\chi_T}$	First order temperature coefficient
η	Ideality factor
S	Illuminated area
P_{inc}	Incident light intensity
g	Interfacial thermal conductance
P	Laser power
μ	Mobility
I_{Ph}	Photocurrent
R	Photoresponsivity
h	Planck's constant
$\mathbf{C_P}$	Specific heat capacity
T	Temperature
k	Thermal conductivity

k_s	Thermal conductivity of supported film
R_m	Thermal resistance
E_v	Valence band
V	Voltage
W	Watt
λ	Wavelength

Preface

Molybdenum disulfide (MoS_2) is a layered transition metal dichalcogenide, which shows tunable bandgap and good thermal transport behaviour along with high absorption coefficient and mechanically flexible nature. These features of MoS_2 make it suitable for use in next generation electronic and optoelectronic devices. This thesis entitled **"CVD Grown Thermal Conducting 2D-MoS_2 Nanostructures for Photodetection and SERS Applications"** is focused on the synthesis of thermal conducting and semiconducting MoS_2 nanostructures via chemical vapour deposition (CVD) technique and their photodetection and Surface-Enhanced Raman Scattering (SERS) applications. We have prepared three different morphologies of MoS_2 nanostructures- horizontally grown interconnected network of few-layer MoS_2 over Si substrate, horizontally grown triangular bi-layer MoS_2 over SiO_2/Si substrate and vertically oriented few-layer (VFL) MoS_2 over Si substrate. We have characterized prepared MoS_2 films by optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) techniques. To confirm the phase and the semiconducting nature of prepared MoS_2, X-ray diffraction (XRD) and Raman spectroscopy techniques have been performed. The semiconducting nature of prepared MoS_2 nanostructures have been confirmed via Photoluminescence (PL) spectroscopy. In the present work, thermal transport behaviour of triangular bi-layer MoS_2 and VFL-MoS_2 has been investigated using optothermal Raman technique. We have calculated the thermal conductivity (k_s) of ~ 42 ± 8 W m^{-1} K^{-1} and interfacial thermal conductance (g) of ~ 1.264 ± 0.128 MW m^{-2} K^{-1} for triangular bi-layer MoS_2 supported over SiO_2/Si substrate. Higher thermal conductivity of ~ 100 ± 14 W m^{-1} K^{-1} has been found for VFL-MoS_2 nanostructure, which can be associated with reduced phonon-defect scattering due to fewer defects and minimal strain in grown VFL-MoS_2 nanostructure. Further, thermal sensitive quantum confinement phenomenon has been observed in above samples by performing temperature dependent PL study, which provides the information about the tunable nature of their bandgap suitable for optoelectronics application.

Based on the thermal conducting and semiconducting nature of prepared MoS_2 nanostructures, we have used these films for photodetection and SERS applications. The CVD grown MoS_2 nanostructures are n-type in nature and hence they form p-n heterojunction with p-type Si substrate. We have successfully demonstrated the photodetection application of interconnected few-layer MoS_2/Si heterojunction and VFL-MoS_2/Si heterojunction. We have observed the photoresponsivity of ~0.1413 A W^{-1} for few-layer MoS_2/Si heterojunction under white light illumination (0.15 mW cm^{-2}) at -2 V bias. Higher photoresponsivity of ~7.37 A W^{-1} has been obtained for VFL-MoS_2/Si heterojunction under green light illumination (0.15 mW cm^{-2}) at -2 V bias, which can be attributed to the strong light absorption, intralayer carrier transport speed, and effective charge separation. Further, SERS application of prepared MoS_2 nanostructures has been investigated to detect organic pollutants- Rhodamine 6G (R6G) and Methyl orange (MO). We have successfully detected R6G dye using all the prepared MoS_2 nanostructures, while MO dye was detected using VFL-MoS_2 nanostructure. The highest detection limit (10^{-10} M concentration for both the dyes) has been observed for VFL-MoS_2 nanosheets over Si as SERS substrate. This high detection limit can be attributed to the enhanced light trapping and effective dye adsorption due to vertical morphology and vibronic-coupling-enabled charge transfer between MoS_2 and organic dyes.

The present thesis has been organized into seven chapters. The consecutive chapters are organized as follows-

Chapter 1 gives a brief introduction to 2D MoS_2 nanostructure along with an overview of the current literature on thermal conductivity measurement, photodetection and SERS applications of MoS_2 nanostructure.

Chapter 2 describes the synthesis process of three different morphologies of MoS_2 nanostructures. A concise overview of the characterization instruments like XRD, SEM, TEM, Raman, PL and AFM, is provided for structural and morphological studies of MoS_2. This chapter also describes the current voltage measurement process and the preparation method of SERS substrate.

Chapter 3 discusses the temperature and power-dependent Raman studies of horizontally grown triangular bi-layer MoS_2 nanosheets over SiO_2/Si substrate and vertically oriented few-layer (VFL) MoS_2 nanosheets over Si substrate. Thermal conductivity calculation using Optothermal Raman technique has been described in detail.

Chapter 4 discusses the thermal sensitive quantum confinement behaviour of triangular bi-layer MoS_2 and VFL-MoS_2 nanostructures. Tunability of bandgap with temperature has been discussed using appropriate models.

Chapter 5 describes the photodetection application of horizontally grown interconnected network of few-layer MoS_2 and VFL-MoS_2 over Si substrate using p-n junction mode under visible light illumination. Different optoelectronic parameters have been obtained and photodetection mechanism has been discussed in this chapter.

Chapter 6 discusses the SERS detection of R6G and MO molecules using prepared different MoS_2 nanostructures. The mechanisms like molecular resonance, excitonic resonance and vibronic coupling enable charge transfer have been discussed in detail.

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