List of Tables

1.1	Summery of different SERS substrate developed by different techniques .	15
2.1	Maximum LSPR field magnitude for uniform height and periodically vary- ing height Au nanopillar structures	42
5.1	Comparison between maximum residue limit of the considered pesticides and minimum detectable concentration of developed SERS substrate	97
7.1	Comparison of different parameters of the developed SERS substrates	127

List of Figures

1.1	Classical wave and quantum particle interpretation of Raman scattering .	3
1.2	Diatomic molecule as amass on spring	3
1.3	Energy level diagram for Rayleigh scattering, Stokes Raman scattering and anti-Stokes Raman scattering	5
1.4	Schematic of a Raman spectrometer	7
1.5	Schematic diagram of generation of localize surface plasmon	10
1.6	Schematic diagram of charge transfer mechanism	12
2.1	Schematic of a periodically varying height gold nanopillar structure patterned on silica (SiO_2) substrate	37
2.2	Simulation result of Au nanopillar for (a) pillars with no height difference and (b) pillars with height difference of 55nm. We maintain fixed pillar diameter of 50 nm and separation of 10 nm for both the situations. (c) Characteristic curve that represents generated LSPR field conditions for Au nanopillar structures at different pillar height differences	38
2.3	Simulation results of the generated LSPR field conditions for different pillar diameters of the proposed periodic Au nanopillar structures. (a) 50 nm, (b) 100 nmand (c) 120 nmpillar diameter. In all the considered cases, we maintain a constant pillar height difference of 55 nm and spacing of 10 nm (d) representing the characteristic curve of LSPR field conditions for	
	different pillar diameter periodically varying height Au nanopillar structures.	40

2.4	Characteristic curve of separation vs maximum field intensity for pillar diameter periodically varying height Au nanopillar structures ranging from	
	50 to 110 nm at a height difference of 55 nm	41
2.5	Characteristic curve representing the LSPR field magnitudes for different incident laser source wavelength for a same periodically varying height Au nanopillar structure.	42
2.6	(a) Schematic diagram of DASAuNP arrangement, (b) characteristic curve of generated LSPR field magnitude vs internanoparticle spacing for differ- ent nanoparticle side length, (c) and (d) Side and top view of FEM simula- tion result of LSPR field distribution obtained by considering dimensions taken from SEM images	44
2.7	(a) Steps involved in fabrication of DASAuNP. (b) Top view of fabricated diagonally aligned squared gold nanopillar, and the inset image shows the enlarge and tilted view of the nanopillars.	45
2.8	Comparison of Raman spectra of RhB between plane silica substrate and DASAuNP substrate. (a) For 1 mM RhB solution on plane silica substrate, the signal was magnified by 20 times (b) For 1 μ M RhB solution on DASAuNP substrate.	47
2.9	SERS spectra of RhB at different concentrations. For all concentrations, the exciting laser of wavelength 785 nm and output power has been kept constant.	48
2.10	Raman spectra of 1 μ M RhB solution at seven different locations on the DASAuNP substrate.	49
3.1	TEM images of chemically synthesized AuNPs of sizes (a) 20nm, (b) 40nm, (c) 60 nm and (d) photograph of synthesized AuNP colloidal solution	56
3.2	FESEM images showing distribution of AuNPs on (a) diatom frustule and (b) EDX data showing the elemental composition of the self-assembled AuNPs on the diatom frustule	57

58	Simulation results showing the LSPR field enhancement in the proposed SERS substrate upon coupling of 785 nm plane polarized light. three different situations are considered: AuNPs assembled (a) on the surface of the diatom frustule, (b) just above the pores of the diatom and (c) inside the pores. (d) Variation in LSPR field magnitude with respect to size of the assembled AuNPs	3.3
59	(a) Scattered Raman spectra for clean diatom frustule, AuNPs assembled diatom and MG treated SERS substrate, (b) comparison of Raman signal intensities of scattered from MG treated plane glass substrate and from the proposed SERS substrate.	3.4
60	Comparison of Raman signal intensities of 2 $\mu{\rm M}$ MG scattered from three different substrates treated with 20 nm, 40 nm and 60 nm AuNPs	3.5
61	Raman signal intensities measured by the spectrometer for different con- centrations of MG from the designed SERS substrate	3.6
62	Back scattered Raman signal intensities of 1 M MG recorded from 10 different locations of the proposed substrate.	3.7
63	Stability study of the proposed SERS substrate through investigating the intensity fluctuations of Raman peaks (808 cm ⁻¹ , 1186 cm ⁻¹ and 1618 cm ⁻¹) for 1 μ M MG treated on it for two weeks	3.8
64	(a) Raman signal intensities scattered from the SERS substrates when treated with different fluoride level concentrations in water. (b) Back scattered Raman signal intensities of 10 μ M fluoride recorded from 10 different locations of the proposed substrate.	3.9

4.1 Schematic representation of the proposed paper based SERS substrate and its application for measuring of Raman signal from Raman active sample. 70

4.2	(a) TEM image of synthesized AgNPs, (b) Photo images of SERS sub- strates fabricated on different GSM papers. The dispersed area of AgNPs varies from 50.26 mm ² to 73.62 mm ² . FESEM images of AgNPs distribu- tion on (c) 75 GSM, (d) 85 GSM, (e) 100 GSM, (f) 140 GSM and (g) 200 GSM substrates. 10 μ L of the synthesized AgNPs colloidal solution was pipetted on each paper substrate. (h) EDX data represent the elements composition on the sensing region of 100 GSM SERS substrate	72
4.3	Simulation result of LSPR field magnitude for different dimensions of sur- face deposited AgNPs on 100 GSM paper substrate. The spacing between the particle are considered to be varying between 30-80nm	74
4.4	Relative Raman signal intensities of (a) MG and (b) R6G scattered from different GSM papers namely 75 GSM, 85 GSM, 100 GSM, 140 GSM and 200 GSM SERS substrate. 10 μ L of both the samples each of concentration 1 μ M has been dispensed on different GSM SERS substrate	75
4.5	Recorded Raman spectra scattered from the substrate for different con- centrations of (a) MG and (b) R6G. These figures also include the Raman signal intensities of the samples scattered from bare paper substrates	76
4.6	(a) Reproducibility characteristics of the developed substrate while BPE has been used as test sample and (b) Signal intensity variation in different locations of the substrate over an area of $5 \text{ mm} \times 5 \text{ mm}$ corresponding to the Raman peak at 1620 cm ⁻¹ .	77
4.7	Time evaluation performance of PVP capped AgNPs (a) and bare AgNPs (b) diffused SERS substrate. MG has been taken as a test sample. Raman peak of MG 1188 cm ⁻¹ is considered for the present study (c) Raman signal intensities variation corresponding to the peaks same peaks of MG while AuNPs are diffused into the paper substrate	78
4.8	Relative Raman signal intiensities scattered from different concentrations of (a) glucose and (b) artificial urine sample solutions	80
5.1	Schematic diagram of the proposed study.	85
5.2	(a) FESEM image of gold coated PVA nano fibre and (b) EDX data show- ing the elemental compositions	86

5.3	(a) Electromagnetic field distribution around the nanofiber and (b) variation generated electric field magnitude for different gold thickness when785 nm plane polarized light is allowed to incident normally on the structure.	87
5.4	A comparison of Raman signal of MG scattered from three different sub- strates namely plane glass substrate, PVA nanofiber coated substrate and gold coated PVA nanofiber substrate	88
5.5	Characteristics curve of variation of scattered Raman signal intensity of MG at 1188 $\rm cm^{-1}$ with the variation of deposited gold layer thickness	89
5.6	Raman signal scattered from developed SERS substrate while different concentrations 10 $\mu{\rm M},$ 1 $\mu{\rm M},$ 100 nM and 10 nM of MG solution are tested.	90
5.7	Back scattered Raman signal intensities of 10 μ M MG recorded from 13 different locations of the proposed substrate.	91
5.8	Raman Signal intensity variation scattered from different locations of the substrate at wavenumber 1214 cm ⁻¹ when BPE is functionalized with the substrate, the mapping is done over an area of 2.5 mm \times 2.5 mm	92
5.9	Stability study of the proposed SERS substrate through investigating the intensity fluctuations of Raman peak (1188 cm ⁻¹) for 1 μ M MG treated on it for 30 days.	93
5.10	Normalized SERS signal intensity variation of MG solution corresponding to Raman peak 1188 cm ^{-1} for the concentrations 0.00734 mg/L to 0.03669 mg/L.	94
5.11	Raman signal of (a) Deltamethrin, (b) Quinalphos and (c) Thiacloprid at different concentration level scattered from the developed SERS substrate upon functionalization of the pesticides.	95
5.12	Raman signal intensity of deltamethrin, quinalphos and thiacloprid mix- ture when these are mixed at different ratio.	96
6.1	Field emission scanning electron microscope (FESEM) image of BRDVD	

substrate. The inset image shows the distribution of AuNPs on the substrate 107

6.2	Comparison of LSPR field magnitude for a single nanoparticle when it is considered on (a) plane polycarbonate substrate and (b) within the channel of BRDVD substrate. The LSPR field magnitude has also been compared when two closely spaced AuNPs are considered on (c) a plane polycarbon- ate substrate and within the channels of BRDVD substrate oriented (d) laterally and (e) along the length of its channel. (f) Generated electric field magnitude variation for different AuNP size when oriented along the length of the channel. The particle spacing are maintained at 10 nm	109
6.3	A comparison of Raman signal of MG scattered from developed SERS substrate, bare DVD and plane glass substrate.	110
6.4	Characteristics curve of variation of scattered Raman signal intensity of MG, when substrate is developed by using three different size AuNPs	111
6.5	Characteristic Raman spectra of (a) MG and (b) BPE, scattered from the BRDVD SERS substrate at different concentrations	112
6.6	SERS signal intensity variation of (a) MG and (b) BPE, corresponding to the signature Raman peaks at 1188 cm ⁻¹ for MG and 1026 cm ⁻¹ for BPE over an area of 2.5 mm × 2.5 mm on the sensing region of the substrate.	113
6.7	Variation SERS signal intensity of MG corresponding to its signature Raman peak 1188 cm^{-1} for the considered period of time	114
6.8	Raman signal characteristics of (a) albumin, (b) creatinine and (c) urea at different concentrations in DI water	116
6.9	Characteristics Raman peaks of artificial urine sample measured by the Raman spectrometer for different concentrations of (a) albumin (b) creatinine and (c) urea present in the sample	117
6.10	Characteristic SERS signal intensities scattered from the mixture of albu- min, creatinine and urea when mixed at (a) same ratio and (b) in different ratio	118
6.11	Normalized SERS signal intensity variation of (a) albumin, (b) creatinine and (c) urea solution corresponding to their signature Raman peaks at cm^{-1} , 1444 cm^{-1} and 1018 cm^{-1} respectively.	119

List of abbreviations

Abbreviation	Meaning
SERS	Surface Enhanced Raman Scattering
DNA	Deoxyribonucleic Acid
RNA	Ribonucleic Acid
EM	Electromagnetic
NIR	Near Infra Red
CE	Chemical Enhancement
LSP	Localized Surface Plasmon
LSPR	Localized Surface Plasmon Resonance
EF	Enhancement Factor
НОМО	Highest Occupied Molecular Orbit
LUMO	Lowest Unoccupied Molecular Orbit
EBL	Electron Beam Lithography
FIB	Focused Ion Beam
NIL	Nanoimprint Lithography
NSL	Nanosphere Lithography
RSD	Residual Standard Deviation
PVD	Physical Vapor Deposition
AAO	Anodic Aluminum Oxide
LoD	Limit of Detection
DVD	Digital Versatile Disc
CCD	Charge Coupled Device
PVC	Polyvinyl Chloride
PDMS	Polydimethylsiloxane
PDDA	Poly(diallyl dimethylammonium
PVS	Polyinylsiloxane
PVA	International Organization for Standardization
BRDVD	Blu-ray Digital Versatile Disc

UV-VIS	Ultraviolet-Visible
BOD	Biological oxygen Demand
DASAuNP	Diagonally Aligned Squared
	Gold Nanopillar
FEM	Finite Element Method
FESEM	Field Emission Scanning
	Electron Microscope
TEM	Transmission Electron Mi-
	croscope
RhB	RhodamineB
R6G	Rhodamine6G
MG	Malachite Green
PVP	Polyvilylpyrrolidone
DI	Deionized
GSM	Gram per Square Meter
BPE	1,2- bis(4-pyridyl)ethylene
ppm	Parts Per Million

List of symbols

Symbol	Meaning	
m	Atomic mass	
K	Bond strength	
x	Displacement	
μ	Reduce mass	
q	Total displacement	
$ u_m$	Frequency of molecular vibration	
M	Dipole moment	
α	Polarizability	
P_0	Power of incident light	
P_s	Power of scattered light	
I_0	Intensity of incident photons	
α_R	Raman cross section	
λ	Wavelength	
E	Electric field	
M_R	Local field induced dipole moment	
P_rad	Power radiated by dipole	
$\epsilon(r)$	Relative dielectric function	
I_{SERS}	SERS signal intensity	
I_R	Raman signal intensity	
I_{REF}	Reference Raman signal intensity	
N_{REF}	Number of molecules within the excitation volume on the reference substrate	
N_{SERS}	Number of molecules within the excitation area on SERS substrate	
С	Concentration of analyte	
N_A	Avogadro's number	

mL	Milliliter
$\mu \mathrm{L}$	Microliter
mg	Milligram
$\mu { m g}$	Microgram
nm	Nanometer
mM	Millimolar
$\mu { m M}$	Micromolar
nM	Nanomolar
V/m	Volt per meter
σ	Standard deviation
S	Slope