DESIGN AND DEVELOPMENT OF SURFACE-ENHANCED RAMAN SPECTROSCOPY ACTIVE SUBSTRATES FOR TRACE ANALYTE DETECTION

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by

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Submitted

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to the

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Dedicated to my parents

Certificate

This is to certify that the thesis entitled **"DESIGN AND DEVELOPMENT OF SURFACE-ENHANCED RAMAN SPECTROSCOPY ACTIVE SUBSTRATES FOR TRACE ANALYTE DETECTION"**, submitted by **VIMARSH AWASTHI** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy**, is a record of the original, bona fide research work carried out by him under our supervision and guidance. The thesis has reached the standards fulfilling the requirements of the regulations related to the award of the degree.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma to the best of our knowledge.

Prof. Satish Kumar Dubey
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Date:
Place:

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Vimarsh Awasthi

Abstract

This thesis primarily focuses on “Surface-enhanced Raman spectroscopy (SERS): Raman introduction, SERS-active substrate development and experimental validation via trace analytical detection”. Due to the fact that molecules exhibit a noticeable rise in their Raman signals when they are linked to or in close proximity to plasmonic nanostructures, the technology of SERS has been developed as a diagnostic/detection tool. This enhancement in the Raman signal happens due to the presence of localized surface plasmon resonance (LSPR) on the structured/roughened metallic surface and some enhancement may be contributed by charge transfer forming complex between analyte and substrate. Therefore, one of the most crucial areas of SERS research is the development of the novel SERS-active substrate with high sensitivity, large-area hotspot, acceptable reproducibility and good stablity.

In this direction, basics of Raman scattering and SERS is discussed in chapter 1. Raman spectrometer setup over optical table, developed for preliminary testing of fabricated SERS-active susbtrates mentioned in this dissertation, is also briefly described in this chapter. Several experimental tools and computational methods have been used in this dissertation which are discussed in chapter 2. Finite-difference time-domain based simulations using Lumerical to design and optimize polarization independent SERS-active substrates i.e. nano-spiral design has been explored in detail in chapter 3. The substrate design is based on 3-D FDTD simulations and is robust, versatile and sensitive even at low concentrations of the analyte. During this numerical study, enhancement factor was calculated using Purcell factor and thereby comparing it with conventional method of fourth power of electric field. Further, various novel fabrication methods have been explored to design and fabricate sensitive, reproducible, large-area hotspot and stable SERS-active substrates using available facilities in our institute.

Chapter 4 deals with the chemical synthesis of gold and silver nanoparticles. By using these synthesised nanoparticles, two SERS active substrates were prepared. In the first substrate, we propose a design of sensitive and easy to fabricate SERS substrate based on chemically synthesized gold nanoparticles dispersed over Au mirror. Proposed substrate is cost-effective, which could be used for on-site analyte detection. Cotinine, tobacco-related biomarker, detection up to 10^{-10} M concentration

has been observed using the proposed substrate. In the second substrate, we present a design of easy to fabricate, flexible and cost-effective SERS substrate constituting of chemically synthesized Ag nanoparticles embedded superficially on hot-melt adhesive (bio-grade quality) commonly referred as glue stick and used as adhesive. We have demonstrated the detection of R6G (20μL) upto 10^{-6} M concentration on our in-house Raman setup using this SERS substrate.

Chapter 5 deals with the fabrication of large-area reproducible novel SERS-active substrate by roughening the thin gold film, deposited through DC sputtering method, on silicon wafer by irradiating it with cold argon plasma at optimized parameters (time, pressure, power). The amplification of Raman signal, via EM enhancement mechanism, using this design was recorded with enhancement factor of $\approx 10^8$ for the most prominent Raman mode. The hotspots were uniformly distributed all over the surface. This ensures easy and quick detection of analytes with a high order of repeatability without the need of probing hotspot via microscope.

Other novel physical fabrication approach, which was explored, to have a sensitive, large-area and nanogap-rich SERS active substrate was by altering a thin gold (Au) film on the unpolished side of a single-side polished silicon wafer by repeated thermal deposition and annealing in an argon environment. This work is described in chapter 6. The repeated thermal deposition and annealing process was compared on both sides of one-sided polished silicon wafer, however the rear side (etched/unpolished side) demonstrated more enhanced Raman signal owing to the larger effective area. The proposed substrate can be fabricated easily having a high density of hotspots distributed uniformly all over the substrate. This ensures easy, rapid and sensitive detection of analytes with a high degree of reproducibility, repeatability and acceptable uniformity. Optimized substrate shows a high degree of stability with time when exposed to the ambient environment for a longer duration of 148 days. The reported substrate can detect up to 10^{-11} M concentrations of TNT and DNT. This substrate also utilised EM mechanism to enhance the Raman signal.

Lastly in chapter 7, molybdenum oxide in combination with gold nano islands was studied to evaluate their performance as hybrid SERS-active substrate and they seem to perform well in trace amount analyte detection. This hybrid substrate contributed to the enhancement of Raman signal not only through localized surface plasmons but also by charge transfer between substrate and analyte. It is highly sensitive, easy to fabricate and reproduce, stable and large-area SERS substrate. The proposed substrate demonstrated detection up to 10^{-11} M and 10^{-10} M concentrations of R6G and TNT molecules, respectively.

In addition to R6G probe molecules, various nitrogenous chemicals were detected during this dissertation work using the above mentioned substrates fabricated via novel approaches. These substrates may find their applications in various fields such as security, narco-analysis, adulterants in food or even biomolecules detection for diagnosis purpose. Chapter 8 discusses the conclusion of the dissertation and future scope of the research work done.

सार

यह थीसिस मुख्य रूप से "सतह-संवर्धित रमन स्पेक्ट्रोस्कोपी (एसईआरएस): रमन परिचय, एसईआरएस-सक्रिय सब्सट्रेट विकास और प्रयोगात्मक सत्यापन ट्रेस विश्लेषणात्मक पहचान के माध्यम से" पर केंद्रित है। इस तथ्य के कारण कि अणु ध्यान देने योग्य प्रदर्शन करते हैं जब वे किसी प्लास्मोनिक नैनोस्ट्रक्चर से जुड़े होते हैं या उसके निकट होते हैं तो उनके रमन संकेतों में वृद्धि होती है, एसईआरएस की तकनीक को निदान/ पता लगाने का उपकरण के रूप में विकसित किया गया है। रमन सिग्नल में यह वृद्धि उपस्थिति संरचित/खुरदरापन धात्विक सतह पर स्थानीयकृत सतह प्लास्मोन अनुनाद (एलएसपीआर) के कारण होती है और कुछ वृद्धि में चार्ज स्थानांतरण विश्लेषण और सब्सट्रेट के बीच कॉम्प्लेक्स बनाना का योगदान हो सकता है। इसलिए, सबसे महत्वपूर्ण में से एक एसईआरएस अनुसंधान का क्षेत्र नवीन एसईआरएस -सक्रिय सब्सट्रेट का विकास है उच्च संवेदनशीलता, बड़े क्षेत्र का हॉटस्पॉट, स्वीकार्य प्रतिलिपि प्रस्तुत करने योग्यता और अच्छी स्थिरता।

इस दिशा में, अध्याय 1 में रमन प्रकीर्णन और एसईआरएस की मूल बातें पर चर्चा की गई है। ऑप्टिकल टेबल पर रमन स्पेक्ट्रोमीटर सेटअप, प्रारंभिक परीक्षण के लिए विकसित किया गया इस शोध प्रबंध में उल्लिखित गढ़े हुए एसईआरएस-सक्रिय सबस्ट्रेट्स का भी संक्षेप में वर्णन किया गया है इस अध्याय में। कई प्रायोगिक उपकरण और कम्प्यूटेशनल विधियाँ हैं इस शोध प्रबंध में उपयोग किया गया है जिसकी चर्चा अध्याय 2 में की गई है। परिमित-अंतर ध्रुवीकरण को डिज़ाइन और अनुकूलित करने के लिए ल्यूमेरिकल का उपयोग करते हुए टाइम-डोमेन आधारित सिमुलेशन स्वतंत्र एसईआरएस -सक्रिय सबस्ट्रेट्स यानी नैनो-सर्पिल डिज़ाइन का पता लगाया गया है अध्याय 3 में विवरण। सब्सट्रेट डिज़ाइन 3-डी एफडीटीडी सिमुलेशन पर आधारित है विश्लेषक की कम सांद्रता पर भी मजबूत, बहुमुखी और संवेदनशील है। दौरान इस संख्यात्मक अध्ययन में, वृद्धि कारक की गणना परसेल कारक का उपयोग करके की गई थी इस प्रकार इसकी तुलना विद्युत क्षेत्र की चौथी शक्ति की पारंपरिक विधि से की गई। इसके अलावा, डिजाइन और निर्माण के लिए विभिन्न नवीन निर्माण विधियों का पता लगाया गया है संवेदनशील, प्रतिलिपि प्रस्तुत करने योग्य, बड़े क्षेत्र वाले हॉटस्पॉट और स्थिर एसईआरएस -सक्रिय सब्सट्रेट हमारे संस्थान में उपलब्ध सुविधाओं का उपयोग करना।

अध्याय 4 सोने और चांदी के नैनोकणों के रासायनिक संश्लेषण से संबंधित है। का उपयोग करके इन संश्लेषित नैनोकणों से दो एसईआरएस सक्रिय सब्सट्रेट तैयार किए गए। में पहला सब्सट्रेट, हम संवेदनशील और निर्माण में आसान एसईआरएस सब्सट्रेट के डिजाइन का प्रस्ताव करते हैं एयू दर्पण पर बिखरे हुए रासायनिक रूप से संश्लेषित सोने के नैनोकणों पर आधारित। प्रस्तावित सब्सट्रेट लागत प्रभावी

है, जिसका उपयोग ऑन-साइट विश्लेषण का पता लगाने के लिए किया जा सकता है। कोटिनीन, तंबाकू से संबंधित बायोमार्कर, 10^{-10} एम सांद्रता तक का पता लगाना प्रस्तावित सब्सट्रेट का उपयोग करके देखा गया है। दूसरे सब्सट्रेट में, हम प्रस्तुत करते हैं निर्माण में आसान, लचीला और लागत प्रभावी एसईआरएस सब्सट्रेट का एक डिज़ाइन रासायनिक रूप से संश्लेषित एजी नैनोकणों को गर्म-पिघल चिपकने वाले पदार्थ पर सतही रूप से एम्बेड किया जाता है (जैव-ग्रेड गुणवत्ता) को आमतौर पर गोंद की छड़ी के रूप में जाना जाता है और चिपकने वाले के रूप में उपयोग किया जाता है। हम हमारे यहां 10^{-6} M सांद्रता तक R6G (20μL) का पता लगाने का प्रदर्शन किया है इस एसईआरएस सब्सट्रेट का उपयोग करके इन-हाउस रमन सेटअप।

अध्याय 5 बड़े क्षेत्र के प्रतिलिपि प्रस्तुत करने योग्य उपन्यास एसईआरएस-सक्रिय के निर्माण से संबंधित है डीसी स्पटरिंग विधि के माध्यम से जमा की गई पतली सोने की फिल्म को खुरदरा करके सब्सट्रेट, सिलिकॉन वेफर पर अनुकूलित मापदंडों पर ठंडे आर्गन प्लाज्मा के साथ विकिरण करके (समय, दबाव, शक्ति). ईएम संवर्द्धन के माध्यम से रमन सिग्नल का प्रवर्धन तंत्र, इस डिज़ाइन का उपयोग करके $\approx 10^8$ के वृद्धि कारक के साथ दर्ज किया गया था सबसे प्रमुख रमन मोड. हॉटस्पॉट सभी जगह समान रूप से वितरित किए गए थे सतह। यह उच्च क्रम के साथ एनालिटिक्स का आसान और त्वरित पता लगाना सुनिश्चित करता है माइक्रोस्कोप के माध्यम से हॉटस्पॉट की जांच की आवश्यकता के बिना पुनरावृत्ति।

अन्य नवीन भौतिक निर्माण दृष्टिकोण, जिसकी खोज की गई, एक संवेदनशील, बड़े क्षेत्र और नैनोगैप-समृद्ध एसईआरएस सक्रिय सब्सट्रेट एक पतले सोने (एयू) को बदलकर था बार-बार थर्मल द्वारा सिंगल-साइड पॉलिश सिलिकॉन वेफर के बिना पॉलिश किए हुए हिस्से पर फिल्म आर्गन वातावरण में जमाव और एनीलिंग। इस कार्य का वर्णन अध्याय 6 में किया गया है. दोनों पर बार-बार थर्मल जमाव और एनीलिंग प्रक्रिया की तुलना की गई एक तरफा पॉलिश सिलिकॉन वेफर के किनारे, हालांकि पीछे की ओर (नक़्क़ाशीदार/बिना पॉलिश किया हुआ)। साइड) ने बड़े प्रभावी क्षेत्र के कारण अधिक उन्नत रमन सिग्नल का प्रदर्शन किया। प्रस्तावित सब्सट्रेट को हॉटस्पॉट के उच्च घनत्व के साथ आसानी से तैयार किया जा सकता है पूरे सब्सट्रेट पर समान रूप से वितरित। यह आसान, तेज़ और संवेदनशील सुनिश्चित करता है उच्च स्तर की प्रतिलिपि प्रस्तुत करने योग्यता, दोहराने योग्यता और स्वीकार्यता वाले विश्लेषणों का पता लगाना एकरूपता. अनुकूलित सब्सट्रेट समय के साथ उच्च स्तर की स्थिरता दिखाता है जब 148 दिनों की लंबी अवधि के लिए परिवेशीय वातावरण के संपर्क में रखा जाता है। रिपोर्ट किया गया सब्सट्रेट टीएनटी और डीएनटी की 10^{-11} एम सांद्रता तक का पता लगा सकता है। यह सब्सट्रेट ने रमन सिग्नल को बढ़ाने के लिए ईएम तंत्र का भी उपयोग किया।

अंत में अध्याय 7 में, सोने के नैनो द्वीपों के साथ संयोजन में मोलिब्डेनम ऑक्साइड था हाइब्रिड एसईआरएस-सक्रिय सब्सट्रेट के रूप में उनके प्रदर्शन का मूल्यांकन करने के लिए अध्ययन किया गया और वे प्रतीत होते हैं ट्रेस राशि विश्लेषण का पता लगाने में अच्छा प्रदर्शन करने के लिए। इस संकर सब्सट्रेट ने योगदान दिया रमन सिग्नल को बढ़ाने के लिए न केवल स्थानीयकृत सतह प्लास्मों के माध्यम से बल्कि सब्सट्रेट और एनालिटे के बीच चार्ज ट्रांसफर द्वारा भी। यह अत्यधिक संवेदनशील, आसान है स्थिर और बड़े क्षेत्र वाले एसईआरएस सब्सट्रेट के निर्माण और पुनरुत्पादन के लिए। प्रस्तावित सब्सट्रेट ने 10^{-11} एम और 10^{-10} एम सांद्रता तक का पता लगाया क्रमशः R6G और TNT अणु।

R6G जांच अणुओं के अलावा, विभिन्न नाइट्रोजनयुक्त रसायनों का पता लगाया गया इस शोध प्रबंध कार्य के दौरान उपरोक्त वर्णित सब्सट्रेट्स का उपयोग करके तैयार किया गया उपन्यास दृष्टिकोण. इन सबस्ट्रेट्स को विभिन्न क्षेत्रों में अपना अनुप्रयोग मिल सकता है सुरक्षा, नार्को-विश्लेषण, भोजन में मिलावट या यहां तक कि बायोमोलेक्यूल्स का पता लगाने के लिए निदान उद्देश्य. अध्याय 8 शोध प्रबंध के निष्कर्ष और भविष्य पर चर्चा करता है किए गए शोध कार्य का दायरा.

Contents

Certificate

Acknowledgements

Abstract

Contents

List of Figures

List of Tables

Abbreviations

Symbols

1 Introduction **1**
- 1.1 Overview . . . 1
- 1.2 Raman Scattering . . . 2
  - 1.2.1 Classical explanation . . . 3
  - 1.2.2 Quantum explanation . . . 6
  - 1.2.3 Raman instrumentation . . . 7
  - 1.2.4 Offshoots of Raman technique . . . 10
- 1.3 Surface-enhanced Raman scattering . . . 18
  - 1.3.1 Surface Plasmons and Localised Surface Plasmons . . . 21
  - 1.3.2 Enhancement mechanisms . . . 24
  - 1.3.3 SERS substrates . . . 26
- 1.4 Motivation . . . 31
- 1.5 Thesis Organisation . . . 32

2 Experimental and Computational methods 35
2.1 Fabrication Techniques 35
2.1.1 Direct Current (DC) sputtering deposition 35
2.1.2 Thermal evaporation deposition 37
2.1.3 Plasma Asher 38
2.1.4 Thermal chemical vapour deposition 39
2.1.5 Furnace Annealing 40
2.2 Characterization Techniques 41
2.2.1 Raman Spectroscopy 41
2.2.2 Scanning Electron Microscopy 41
2.2.3 Atomic Force Microscopy 43
2.2.4 UV-Visible Spectroscopy 45
2.2.5 X-ray Photoelectron Spectroscopy 46
2.2.6 X-Ray Diffraction 47
2.3 Computational Methods 48
2.3.1 Finite-Difference Time-Domain method 48

I Numerical design of SERS substrate 51

3 Design of polarization independent SERS substrate with Raman gain evaluated using Purcell factor 53
3.1 Summary 53
3.2 Introduction 54
3.3 Numerical Design 57
3.4 Results and Discussion 58
3.4.1 Tolerance Analysis with respect to the angle of inclination of the source 64
3.4.2 Purcell factor and Raman Gain 67
3.4.3 Tolerance Analysis with respect to the design parameters . . . 69
3.5 Conclusion 69

II Fabrication of novel SERS substrates 73

(a) Chemical fabrication approach 77

4 SERS substrates fabricated using chemically synthesized Ag/Au nanoparticles 77
4.1 Summary 77
4.2 Introduction 78
4.3 Experimental Details 80
4.3.1 Materials 80

4.3.2 Synthesis of gold nanoparticles . . . 81
4.3.3 Synthesis of silver nanoparticles . . . 82
4.3.4 FDTD simulations . . . 82
4.4 Results and Discussion . . . 83
4.4.1 Characterization of synthesised nanoparticles . . . 83
4.4.2 Nanoparticles coated Au mirror as SERS substrate . . . 84
4.4.3 Flexible SERS substrate . . . 88
4.5 Conclusion . . . 90

(b) Physical fabrication approach **95**

5 Detection of nitrogenous and nitro-aromatic compound with thin gold films roughened by cold Argon plasma as SERS-active substrate **95**
5.1 Summary . . . 95
5.2 Introduction . . . 96
5.3 Experimental Section . . . 99
5.3.1 Chemicals and materials . . . 99
5.3.2 Preparation of Au thin films . . . 99
5.3.3 Plasma treatment . . . 100
5.3.4 Characterization of roughened Au thin films . . . 100
5.3.5 SERS measurements . . . 101
5.4 Results and Discussion . . . 101
5.4.1 Optimization of SERS substrate: . . . 102
5.4.1.1 Purity of SERS substrate: . . . 102
5.4.1.2 SERS measurements: . . . 103
5.4.1.3 Morphology of SERS substrate: . . . 104
5.4.1.4 FDTD simulations and Raman mapping: . . . 105
5.4.2 Performance Analysis of SERS substrate: . . . 108
5.4.2.1 Sensitivity: . . . 108
5.4.2.2 SERS signal stability: . . . 109
5.4.2.3 Repeatability: . . . 111
5.4.2.4 Detection of PNBA: . . . 111
5.5 Conclusion . . . 113

6 Nanogap-Rich SERS-active Substrate Based on Double-step Deposition and Annealing of Au Film over Back Side of Polished Si **117**
6.1 Summary . . . 117
6.2 Introduction . . . 118
6.3 Experimental section . . . 121
6.3.1 Materials and chemicals . . . 121
6.3.2 Preparation of SERS substrate . . . 121

    - 6.3.3 Characterization of the fabricated substrate 122
    - 6.3.4 SERS measurements 122
    - 6.3.5 Numerical analysis of Electric fields 123
  - 6.4 Results and Discussion 123
    - 6.4.1 SERS substrate optimization 124
    - 6.4.2 Efficiency analysis of optimized SERS-active substrate 129
      - 6.4.2.1 Uniformity: 129
      - 6.4.2.2 Stability: 132
      - 6.4.2.3 Sensitivity: 134
  - 6.5 Conclusion 138

(c) Confluence of chemical and physical fabrication approach **143**

7 Gold-nanoislands decorated α-MoO$_3$ flakes hybrid utilising defect engineering via thermochromic characteristics as sensitive SERS-active substrate **143**
  - 7.1 Summary 143
  - 7.2 Introduction 144
  - 7.3 Experimental details 147
    - 7.3.1 Materials 147
    - 7.3.2 Instruments 148
    - 7.3.3 Preparation of SERS substrate 148
      - 7.3.3.1 Growth of α-MoO$_3$ micro-flakes: 148
      - 7.3.3.2 Au coating: 148
      - 7.3.3.3 Annealing of Au-coated MoO$_3$ microflakes: 149
    - 7.3.4 SERS measurements 149
  - 7.4 Results and discussion 150
  - 7.5 Conclusion 160

8 Conclusion and Future scope **163**
  - 8.1 Conclusion 163
  - 8.2 Future scope 166

A Detection of nitrogenous and nitro-aromatic compound with thin gold films roughened by cold Argon plasma as SERS-active substrate **169**
  - A.1 Roughness analysis of plasma etched substrate with different parameters: 169
  - A.2 Argon plasma etching of gold thin film of thickness 20nm, 50nm and 100nm: 171

A.3 Raman spectra of silicon substrate, 10^{-1} M urea over silicon substrate and 10^{-1} M PNBA over silicon substrate: 171

B Nanogap-Rich SERS-active Substrate Based on Double-step Deposition and Annealing of Au Film over Back Side of Polished Si 173

C Gold-nanoislands decorated α-MoO$_3$ flakes hybrid utilising defect engineering via thermochromic characteristics as sensitive SERS-active substrate 179

Bibliography 183

List of Publications 223

Author's Biography 227

List of Figures

1.1 Energy level diagram showing Raman and Rayleigh scattering 3
1.2 Schematic of experimental set-up of Raman scattering 9
1.3 Photo of experimental set-up of Raman scattering 10
1.4 Jablonski energy level diagram showing transactions involved in different Raman techniques 11
1.5 Schematic of TERS 14
1.6 Schematic of time-gated Raman spectroscopy setup 16
1.7 Schematic of Optical tweezer Raman spectroscopy setup 17
1.8 Surface-enhanced Raman scattering (SERS) as higher order Raman scattering. (a) Sketch of a plasmon-enhanced Raman process relevant for SERS. The steps are (1) excitation of a plasmon by the incoming light ω_L; (2) molecular transition from ground state g to intermediate state i by coupling to the plasmonic near field; (3) molecular relaxation to final state f and excitation of the plasmon; (4) emission of Raman-scattered light ω_S by the plasmon; (b) Plasmon-enhanced Raman process in (a) illustrated as a Feynman diagram, which corresponds to fourth-order perturbation theory; (c) Feynman diagrams of three other scattering processes that are relevant for SERS, that is, (i) only the incoming light or (ii) only the Raman-scattered light couples to the plasmon and (iii) the Raman process without plasmonic enhancement 20
1.9 (a) Surface plasmon polaritons (SPPs) at the interface of dielectric and metal; (b) dispersion relation of SPPs; (c) evanescent fields in the two half spaces [1] 23
1.10 (a) EM enhancement (b) CM enhancement 25
1.11 Methodology followed in a typical lithographic process 30
1.12 (a) Lithographically prepared nanopatterns (b) Chemically synthesised nanoparticles 31

2.1 Photo of DC sputtering system at NRF, IITD 36
2.2 Schematic diagram of thermal evaporation system 37
2.3 Photograph of thermal evaporation system 38
2.4 Photograph of plasma asher system at NRF, IITD 39
2.5 Schematic of thermal CVD to grow MoO_3 flakes 40

2.6 (a) Photograph and (b) schematic of thermal furnace used for annealing 41
2.7 Photograph of Renishaw Raman microscope 42
2.8 Schematic of SEM 43
2.9 Schematic of AFM 44
2.10 Schematic representation of UV-Vis spectroscopy 45
2.11 Schematic representation of (a) photoelectric effect (b) XPS instrument 46
2.12 Schematic representation of XRD principle 47

3.1 (a) 3D view of CAD model of the proposed nano-spiral structure (inset shows the spiral structure) (b) refractive index profile of nano-spiral (blue colour indicates gold, red colour indicates blood) (c) magnified view of the nano-spiral indicating the various design parameters . . . 57
3.2 Electric field strength profile at stokes wavelength $\lambda = 763$ nm using monochromatic Gaussian source, $\lambda = 660$ nm for excitation for the pattern illustrated in Fig. 3.1(a). The color bar shows the electric field enhancement, normalized to the amplitude of the incident electric field. (a) electric field strength on the surface of gold nano-spiral (b) cross-sectional view of the electric field strength. 60
3.3 Spectrum showing plasmon resonant wavelength of the proposed design 61
3.4 Electric field strength profile at Stokes wavelength $\lambda = 763$ nm using monochromatic Gaussian source, $\lambda = 660$ nm for excitation. The colour bar shows the electric field enhancement, normalized to the amplitude of the incident electric field. (a) Electric field strength when light is polarized at 90°(b) Electric field strength when sample is kept in the reflection mode. 62
3.5 (a) Electric field strength profile at Stokes wavelength $\lambda = 798$ nm using monochromatic Gaussian source, $\lambda = 700$ nm for excitation, when urea is used as an analyte (b) Electric field strength profile at Stokes wavelength $\lambda = 744$ nm using monochromatic Gaussian source, $\lambda = 680$ nm for excitation, when water is used as an analyte. The colour bar shows the electric field enhancement, normalized to the amplitude of the electric field. 65
3.6 Tolerance analysis with respect to incident angle of source. 66
3.7 Electric field strength profile at stokes wavelength, $\lambda = 763$ nm using monochromatic Gaussian source, $\lambda = 660$ nm inclined at an angle of 25°for excitation. The colour bar shows the electric field enhancement, normalized to the amplitude of the incident electric field. 66

4.1 Photograph of colloidal solution of synthesised gold nanoparticles . . 81
4.2 Photograph of colloidal solution of synthesised silver nanoparticles . . 82
4.3 (a) TEM image of Au NPs (b) FESEM image of Au NPs (c) Size distribution of Au NPs (d) UV-Visible spectra of Au NPs 83
4.4 (a) High resolution Transmission electron microscopy (HRTEM) image (b) UV-Visible spectra of synthesized Ag NPs 84

4.5 Schematic of Au mirror based SERS substrate 85
4.6 Simulated E-field profile (a)without Au mirror (b) with Au mirror (c) Comparison of EF 86
4.7 SERS spectra of (a) 10^{-4} M R6G over different combinations of Au/Ag mirror and Au NPs (b) 10^{-4} M, 10^{-5} M, 10^{-6} M R6G over Au NP coated Au mirror at excitation wavelength of 785nm 86
4.8 SERS spectra of cotinine with 10^{-6} M to 10^{-10} M concentration and calibration curve plotted between SERS intensity of 1032 cm^{-1} Raman mode with logarithmic concentration 87
4.9 SERS spectra of TNT with 10^{-6} M to 10^{-9} M concentration 88
4.10 Schematic of the substrate used in this study 89
4.11 SERS spectra of R6G with 10^{-5} M and 10^{-6} M concentration 90

5.1 Schematic of SERS-active substrate fabrication and SERS signal measurements 102
5.2 EDS spectra of SERS substrate with weight and atomic percent present in the substrate 103
5.3 SERS spectra of Urea over argon plasma treated Au film coated silicon substrate with (a)10^{-4} M Urea with parameters: pressure-0.2mbar power-300W at different time (b) 10^{-4} M Urea with parameters: time-3 min pressure-0.2mbar at different power (c) 10^{-4} M Urea with parameters: time-3 min power-300W at different pressure 104
5.4 FESEM images of argon plasma treated Au thin films with their grain size distribution histogram fitted with Gaussian curve at following parameters: 0.1mbar, 0.2mbar, 0.3mbar pressure with 300W power and 180s time 106
5.5 Simulated electric field profile in the gap between the gold nanoparticles with different size and varying gap when excited by monochromatic Gaussian beam of λ=785nm propagating in z direction (a1-a3) Au nanoparticles with size=48 nm and gap variation 3 nm, 6 nm and 9 nm respectively (b1-b3) Au nanoparticles with size=65 nm and gap variation 3 nm, 6 nm and 9 nm respectively (c1-c3) Au nanoparticles with size=75 nm and gap variation 3 nm, 6 nm and 9 nm respectively 107
5.6 2D Raman map of 10^{-4} M urea coated argon plasma etched gold thin films for 1129 cm^{-1} and 1615 cm^{-1} peaks respectively 108
5.7 SERS spectra for different concentration of Urea over optimized substrate. (1,2) Calibration curve of urea, showing relation between SERS intensity at 1129 cm^{-1} and 1615 cm^{-1} as a function of logarithmic urea concentration. The linear part of the calibration curve is in the inset with R^2 values for linear fitting. 109

5.8 SERS spectra of 10^{-4} M Urea over the optimized plasma etched/treated Au thin film against number of days after the sample preparation. Inset: Plot showing relation between SERS intensity for 1615 cm^{-1} peak with number of days after which signal is taken. 110
5.9 SERS spectra of 10^{-4}M Urea over plasma treated Au thin film at following parameters: 3min 300W 0.2mbar at different location of the same substrate. 112
5.10 SERS spectra of PNBA over plasma ashered Au thin film at following parameters: 3min 300W 0.2mbar at different concentrations. (1,2) Calibration curve of PNBA, showing relation between SERS intensity at 1179 cm^{-1} and 1349 cm^{-1} as a function of logarithmic concentration R^2 values for linear fitting. 113

6.1 Methodology followed for SERS substrate fabrication 121
6.2 SERS spectra of 10^{-5} M R6G on (a) front side (b) back side of single-side polished silicon substrate at 785 nm excitation laser (c) Intensity comparison of 1369 cm^{-1} Raman mode for polished and unpolished side of single-side polished silicon substrate. 125
6.3 SEM images of all the fabricated substrates with corresponding name in the inset. 127
6.4 UV-Vis spectra for F(10), F(10+10), B(10), B(10+10) samples . . . 128
6.5 FESEM image of (a) F(10) (b) F(10+10) (c) B(10) (d) B(10+10) samples with (a1-d1) corresponding E-field distribution and (a2-d2) nano-island size distribution histogram. 130
6.6 Uniformity in SERS signal when collected from 10 randomly chosen places of same sample i.e., B(10+10). R6G of 10^{-5}M concentration used as analyte. 132
6.7 2D Raman mapping images of 10^{-5} M R6G coated substrate for (a) 1366 cm^{-1} and (b) 1507 cm^{-1} Raman modes, respectively. (c) Raman spectra of each pixel in the measured region. 133
6.8 Stability in SERS signal of 10^{-5} M R6G over the optimized substrate compared to number of days after SERS-active substrate fabrication. Inset plot shows the relation between SERS signal intensity for 1514 cm^{-1} Raman mode of R6G with number of days. 134
6.9 SERS spectra of TNT with 10^{-5} M to 10^{-11} M concentration on back side of single-side polished silicon substrate at 785 nm excitation laser 136
6.10 SERS spectra of DNT with 10^{-5} M to 10^{-11} M concentration on back side of single-side polished silicon substrate at 785 nm excitation laser 137

7.1 Schematic diagram for the fabrication of Au nano-island decorated MoO_3 flakes via chemical vapor deposition of MoO_3 flakes followed by thermal evaporation of thin gold film and subsequent annealing in an argon environment. 147

7.2 FESEM images of (a1-a3) MoO_3 microflakes, (b1-b3) MoO_3 microflakes annealed at 350°C in argon environment and (c1-c3) gold nanoisland decorated MoO_3 microflakes, with different magnification 151

7.3 (a) X-ray diffractogram and (b) Raman spectra of pristine MoO_3, annealed MoO_3 and Au nano-island decorated MoO_3 153

7.4 The wide-range XPS survey spectrum of (a) pristine MoO_3 flakes and (d) annealed MoO_3 flakes. The deconvoluted spectra of Mo 3d on the surface of (b) pristine MoO_3 flakes and (e) annealed MoO_3 flakes. The deconvoluted spectra of O 1s on the surface of (c) pristine MoO_3 flakes and (f) annealed MoO_3 flakes. 155

7.5 (a) UV-Vis absorbance spectra of pristine MoO_3 flakes, annealed MoO_3 flakes and Au-decorated MoO_3 flakes. (b) SERS spectra of 10^{-5} M R6G over various substrates at 514 nm excitation wavelength. 157

7.6 (a) SERS spectra of R6G with 10^{-6} M to 10^{-11} M concentration at 514 nm excitation laser (20 s time, 1% laser power, 2 accumulations) (b) Calibration curve for 1642 cm^{-1} Raman mode intensity with respect to R6G concentration (ng/L) on logarithmic scale. (c) SERS spectra of 10^{-6} M R6G over 50 points on Au-decorated MoO_3 flakes with (d) histogram showing intensity variation of 1355 cm^{-1} Raman mode. . . 158

7.7 SERS spectra of TNT with 10^{-6} M to 10-10 M concentration at 514 nm excitation laser (20 s time, 5% laser power, 2 accumulations) (b) Calibration curve for 1355 cm^{-1} Raman mode intensity with respect to logarithmic TNT concentration (ng/L). 160

A.1 2D AFM images of the substrates mentioned in Table A.1 170

A.2 2D AFM images of the 20nm, 50nm and 100nm substrates etched by argon plasma at following parameters: power-300W, pressure-0.2mbar, time- 300s 171

A.3 Raman spectra of silicon substrate, 10^{-1} M urea and 10^{-1} M PNBA 172

B.1 SEM image of unpolished surface of one-side polished boron-doped p-type single crystal silicon wafer of prime grade (Czochralski (CZ) grown) with ≺100≻ orientation. 173

B.2 Optical image of (a) Unpolished silicon (b) Etched side of n-type ≺100≻ oriented one-side polished silicon substrate (c) Etched side of p-type ¡100¿ oriented one-side polished silicon substrate. 174

B.3 FESEM images showing side view of B(10+10), B(20+10) and B(30+10) 174

B.4 Cross-sectional view of optimized substrate i.e. B(10+10) (a) shows the side view which indicates the roughness of etched surface (b) zoom out view of portion of nano-islands formed on slant surface of unpolished substrate (c) more zoomed view indicating high nano-island density (d) top close view of edges on rear side of substrate (e-f) zoom out top view image of rectangular facets showing dense nano-islands. 175

B.5 Raman spectra of 10-8 M concentration of TNT and DNT over bare silicon. . . . 177

C.1 EPMA-WDS elemental mapping of pristine MoO_3 and annealed MoO_3 180
C.2 Optical bright field images of MoO_3 flakes grown on silicon substrate 180
C.3 EDS spectra of gold nanoisland decorated MoO_3 microflakes. Electron image shows the top-view area of which EDS spectra is taken. . 181
C.4 GIXRD spectra of pristine MoO_3, annealed MoO_3 and Au nano-island decorated MoO_3. . . . 181
C.5 Bandgap calculation of a pristine α-MoO_3 flakes using Kubelka–Munk (K–M) function. . . . 182
C.6 SERS spectra of (a) 10^{-6} M R6G (b) 10^{-7} M TNT at 785 nm excitation laser (40 s, 100%, 3 acquisitions) over gold decorated MoO_3 flakes. . . . 182

List of Tables

3.1 Tolerance analysis with respect to different design parameters 70

5.1 Comparison with reported SERS detection method 114

A.1 AFM analysis showing roughness of the Au-film after being treated with Argon plasma under different conditions of time, power and pressure. 170

Abbreviations

SERS	**S**urface **E**nhanced **R**Raman **S**pectroscopy
EF	**E**nhancement **F**actor
EM	**E**lectromagnetic **E**nhancement
CM	**C**hemical **E**nhancement
SPR	**S**urface **P**lasmon **R**esonance
LSPR	**L**ocalised **S**urface **P**lasmon **R**esonance
CVD	**C**hemical **V**apour **D**eposition
PICT	**P**hoto **I**nduced **C**harge **T**ransfer
AFM	**A**tomic **F**orce **M**icroscopy
XPS	**X**-ray **P**hotoelectron **S**pectroscopy
SEM	**S**canning **E**lectron **M**icroscopy
FESEM	**F**ield **E**mission **S**canning **E**lectron **M**icroscopy
EDS	**E**lectron **D**ispersive **S**pectroscopy
FDTD	**F**inite **D**ifference **T**ime **D**omain
PML	**P**erfectly **M**atched **L**ayers
R6G	**R**hodamine 6G
PNBA	**p** p-nitrobenzoic acid
TNT	2,4,6-**t**ri**n**itro**t**oluene
DNT	2,4 **d**i**n**itro**t**oluene
QCM	**Q**uartz **C**rystal **M**icrobalance
LOD	**L**imit **O**f **D**etection
LOQ	**L**imit **O**f **Q**uantification

Symbols

F_P	Purcell factor
Q	quality factor
ω	angular frequency
c	speed of light in vacuum
λ	wavelength
ϵ	dielectric constant/permittivity
ν	frequency
k_0	wavevector in free space
$\hbar$	reduced Planck‘s constant
n_{eff}	effective index