**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.