ABSTRACT

Surface Enhanced Raman Spectroscopy (SERS) has become a powerful method for detection of diverse analytes ranging from solution of picomolar concentration to single molecule and single cell analysis. The distinctive nature of SERS technique comes from the resonance of surface plasmons of metal nanostructure due to oscillating electric field of the incident laser. Surface plasmon resonance results in enhanced electric field or hotspots in the vicinity of metal structure which results in amplified Raman signal. Optimum hotspots on SERS substrate are achieved by fabricating appropriate metal nanostructures. Efficacy of the nanostructures depends on efficient excitation of plasmon resonance and interaction of the plasmons with its adjacent environment. Hence, substrate with favorable optical property would aid in pushing the limits of detection. Recent development in biosensors for qualitative and quantitative detection using SERS technique involves precise engineering in fabrication of SERS substrates. The requirement of a fixed SERS platform, instead of conventional metal nanoparticle colloid, is preferred in a Lab-on-a-chip (LOC) system. This thesis focuses on exploring substrate effects on surface plasmon resonance of metal nanostructure. In the process, large area SERS substrates have been fabricated for detection of various analytes. One of such substrates has been integrated with centrifugal microfluidic (CMF) system.

In this work, plasmon-substrate interaction has been studied elaborately using analytical models and computational tools. Silver nanoparticles have been fabricated on Si substrate by sputtering. Optical properties of the substrate have been modified by depositing SiO_2, HfO_2 and Si_3N_4 films of varying thickness. Non-radiative and radiative interactions have been observed prominently in SERS spectra which correlate with the optical property of the substrate. The most effective interaction has been the energy transfer between the plasmons and the polarization charges of the base Si substrate. These serve as guidelines to fabricate, modify and improve large area SERS substrates.

Anodized Aluminum Oxide Template (AAOT) and Germanium Nanowire (GeNW) have been fabricated and subsequently coated with thin silver film for application in SERS as large area substrate. Anodization of Al thin film has been studied with varying fabrication parameters. Resulting nanopores have been coated with Ag and the evolution of silver film on the template has been observed. Optimized Ag structures show enhanced performance depending on the location of the hotspots on these substrates.

Extensive experiments have been carried out to understand vapour-liquid-solid (VLS) growth of Si and Ge nanowires using plasma enhanced chemical vapour deposition (PECVD) technique with precise control over the length of the NWs. GeNWs with dielectric shell were coated with Ag film and AgNPs. Subsequently, the efficacy of the SERS substrates was compared. Aforementioned plasmon-substrate interactions have been observed in the characterization results of the large area substrates. However, tuning of these substrates for a specific wavelength is extremely complex. This brings the requirement of an ideal substrate possessing the following properties:

i. Scalable fabrication process
ii. Ease of tunability for any wavelength
iii. High shelf life

Hence, silver nano-buds have been fabricated to address the issues. Silver structures are fabricated on the tip of GeNWs through galvanic displacement reaction. An optimization technique has been developed to tune the substrate to any wavelength in real time. The analytical enhancement factors remain close to 10^5 for a wide range of wavelengths which is comparable to some of substrates fabricated by e-beam lithography. GeNW substrates do not require any specific packaging and silver can be formed easily on the substrates on demand. This substrate also addresses the most important issue of shelf life. Ag nano-bud substrate has been subsequently used in an integrated SERS microfluidic system for analysis of blood components.

Centrifugal microfluidic (CMF) devices have been developed for plasma and cell separation from whole blood. A valving mechanism was developed to manipulate fluid flow on the same CMF disc which enables integration of multiple microfluidic networks. Later, soft lithography process has been modified to incorporate silver nano-bud SERS substrate in the CMF disc. Thus, a complete integrated CMF-SERS device has been fabricated. This does not require fabrication of SERS active site either on PDMS or on glass. Prefabricated SERS substrate has been used to accomplish this which has drastically reduced the process steps and complexity as compared to other methods reported in literature. As a proof-of-concept, SERS substrate has been integrated with plasma separation device and SERS spectrum has been obtained for plasma.