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14. ABSTRACT
Traditionally, most of the fabrication, assembly and testing of plasmonic nanostructures for surface enhanced Raman scattering (SERS) substrates has pertained to static substrates such as glass and silicon. However, these static substrates severely limit the application of plasmonic nanostructures as (i) they provide no means to alter the state of assembly of the nanostructures once they are formed or anchored on the surface i.e., not reconfigurable and (ii) preclude applications which demand non-planar, flexible or conformal surfaces. The above considerations has

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Report Title

Final Report: Flexible SERS Substrates: Challenges and Opportunities

ABSTRACT

Traditionally, most of the fabrication, assembly and testing of plasmonic nanostructures for surface enhanced Raman scattering (SERS) substrates has pertained to static substrates such as glass and silicon. However, these static substrates severely limit the application of plasmonic nanostructures as (i) they provide no means to alter the state of assembly of the nanostructures once they are formed or anchored on the surface i.e., not reconfigurable and (ii) preclude applications which demand non-planar, flexible or conformal surfaces. The above considerations has led to the development of a novel class of SERS substrates based on flexible substrates such paper, polymer membranes and electrospun fibers. The workshop hosted a diverse set of scientists and engineers from academia, government and industry to identify the most critical challenges and potential opportunities in this exciting field. The workshop served as a forum to review the recent progress and exchange ideas amongst the participants with diverse research backgrounds. The workshop involved oral presentations from the principal investigators showcasing their recent work in the field and poster presentations from graduate students. A significant fraction of the time was dedicated to panel discussion to identify the most critical issues that need to be addressed.

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(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

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Number of Manuscripts:

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TOTAL:

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TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Saide Z Nergiz	0.25	
FTE Equivalent:	**0.25**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

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Total Number:	

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The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

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Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME	
Saide Nergiz	
Total Number:	1

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

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Scientific Progress

The workshop, entitled Flexible SERS substrates: Challenges and Opportunities, hosted a diverse set of scientists and engineers from academia, government and industry to identify the most critical challenges and potential opportunities in this exciting field. The workshop served as a forum to review the recent progress and exchange ideas amongst the participants with diverse research backgrounds. The workshop involved oral presentations from the principal investigators showcasing their recent work in the field and poster presentations from graduate students. A significant fraction of the time was dedicated to panel discussion to identify the most critical issues that need to be addressed.

Technology Transfer

Title: Flexible SERS substrates: Challenges and Opportunities

Organizer: Srikanth Singamaneni, Department of Mechanical Engineering and Materials Science and Institute of Materials Science and Engineering, Washington University in St. Louis, Missouri 63130, USA

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Email: singamaneni@wustl.edu, PH: 314-935-5407

Time and location: June 25 and 26th, Washington University in St. Louis, St. Louis

Topics covered in the workshop:

1. Computational electromagnetics in plasmonics and SERS
2. Advances in the design, synthesis and fabrication of plasmonic nanostructures
3. Biological recognition elements for chemically selective SERS substrates
4. Unconventional SERS substrates design, fabrication (e.g., writing, printing on paper substrates) and applications.
5. Advances in Raman instrumentation (Portable and field-deployable)
6. Reporting standards in SERS-based chemical sensors

Summary: Traditionally, most of the fabrication, assembly and testing of plasmonic nanostructures for surface enhanced Raman scattering (SERS) substrates has pertained to static substrates such as glass and silicon. However, these static substrates severely limit the application of plasmonic nanostructures as (i) they provide no means to alter the state of assembly of the nanostructures once they are formed or anchored on the surface *i.e.*, not reconfigurable and (ii) preclude applications which demand non-planar, flexible or conformal surfaces. The above considerations has led to the development of a novel class of SERS substrates based on flexible substrates such paper, polymer membranes and electrospun fibers. These flexible SERS media based on unconventional substrates such as paper offer distinct advantages compared to the conventional SERS substrates in that (i) flexible nature of the substrate enables conformal contact with the surfaces under investigation leading to efficient sample collection; (ii) porous nature of the SERS substrate (interstices between the fibers) provides efficient access to the analytes; (iii) high surface area of the 3D paper substrate results in large dynamic range of the chemical sensors; (iv) intricate network of fibers decorated with metal nanoparticles can provide potentially high density of electromagnetic hotspots and (v) intense light scattering caused by the fibrous structure of the substrate (e.g., paper) enables efficient light-metal interaction; (vi) facile

fabrication leads to efficient, robust, reliable, reusable and cost-effective SERS substrate-s.

While the preliminary efforts in this direction appear promising, numerous challenges need to be overcome to realize an ideal SERS substrate with most of the attributes mentioned above: (i) improve the SERS enhancement uniformity across the substrate and from substrate to substrate to realize a relative standard deviation (RSD) of less than 10% over a 10 inch^2 substrate through rational choice of commercial paper substrate or through novel paper processing methodologies (ii) overcome inherently poor chemical specificity of unmodified plasmonic nanostructures and hence poor chemical selectivity of SERS substrates by integrating biomimetic approaches with SERS substrates (iii) simplify and standardize nanostructure printing approaches to realize multiplexed SERS substrates and (iv) imparting multifunctionality to SERS substrates to achieve separation, preconcentration and detection on flexible SERS substrates. Clearly, progress along this direction will require interdisciplinary efforts involving analytical chemists, materials chemists, materials engineers, biologists, and bioengineers.

The workshop hosted a diverse set of scientists and engineers from academia, government and industry to identify the most critical challenges and potential opportunities in this exciting field. The workshop served as a forum to review the recent progress and exchange ideas amongst the participants with diverse research backgrounds. The workshop involved oral presentations from the principal investigators showcasing their recent work in the field and poster presentations from graduate students. A significant fraction of the time was dedicated to panel discussion to identify the most critical issues that need to be addressed. Below we list the oral presentations at the workshop with the abstracts:

Microfluidics and SERS for High performance Sample Capture and Analysis

Carl Meinhart

Microfluidic devices enable rapid and cost effective chemical analysis of small quantities of sample. We have developed microfluidic systems that allow for the detection of many types of analytes, whether airborne or in complex samples, based on surface-enhanced Raman spectroscopy (SERS).

Nearly all microfluidic devices to date consist of some type of fully-enclosed microfluidic channel. The concept of ‘free-surface’ microfluidics has been pioneered at UCSB during the past several years, where at least one surface of the microchannel is exposed to the surrounding air. Surface tension is the dominating force at the micron scale, which can be used to control effectively fluid motion.

There are a number of distinct advantages to the free surface microfluidic architecture. For example, the free surface provides a highly effective mechanism for capturing certain low-density vapor molecules. This mechanism, in combination with SERS, was used to develop a novel explosives vapor detection platform, which is capable of sub part-per-billion sensitivity with high specificity.

In another application, we have developed a microfluidic device that detects trace concentrations of drugs of abuse in saliva within minutes using SERS. Its operation was demonstrated using methamphetamine. The detection scheme exploits concentration gradients of chemicals, fostered by the laminar flow in the device, to control the interactions between the analyte, silver nanoparticles, and a salt. This system has also been applied to detection of trace antibiotics for food safety applications and several other analytes.

Rapid, Cost-Effective, and Reproducible SERS Substrates based on Stamped Nanoporous Gold

Sharon M. Weiss

In this talk, an easy-to-fabricate, uniform, and sensitive SERS-active substrate that combines the self-organized and highly interacting nanoscale morphology of nanoporous gold with the advantages of reproducibly nanopatterned periodic structures will be discussed.

A straightforward process is utilized to stamp two-dimensional square grating patterns in nanoporous gold films. Through appropriate tuning of the materials properties and grating parameters, both the localized surface plasmon and propagating surface plasmon contribute to the SERS signal enhancement. Uniform SERS substrates without hot spots are demonstrated with SERS enhancements near 108 compared to non-enhancing substrates for the detection of benzenethiol. The design methodology, fabrication, and characterization of the patterned nanoporous gold SERS substrates will be reported in detail along with future prospects for specific chemical functionalization and incorporation as flexible substrates.

Nanoimprint Lithography of 3-D Structures for SERS Sensor

Wei Wu

Nanoimprint lithography (NIL) is a cost-effective nano-patterning technology based on the mechanical deformation of a resist. During the process, 3-D information of the mold are transferred to the resist, in contrast, most other lithography technologies only transfer 2D information to the resist. We developed a process to fabricate high- aspect-ratio 3-D nanostructures using nanoimprint lithography. For example, we reported the fabrication of nano-cones with height up to 2 nm and tip diameter less than 15 nm and nano-pillar array with 100 nm in diameter and 750 nm in height.

By adding Gold nano-particles to those 3D nanostructures, we demonstrated several molecule trapping sensing devices based on surface-enhanced Raman Spectroscopy (SERS). The 3D NIL process provides a cost-effective method for mass production of such SERS substrates reliably and deterministically for sensor applications, and opens a path toward the future integration of such SERS substrates with optical elements as well as MEMS components.

Surface-Enhanced Raman Spectroscopy to Study Single Molecules and Supramolecular Assemblies in Well-Defined Environments

Yuebing Zheng

Single-molecule measurements and control of functional molecules on surfaces under ambient environments are essential, but currently difficult, aspect of nanoscience and nanotechnology. The difficulty arises from poorly controlled molecule-substrate and intermolecular interactions in heterogeneous surface environments. We have employed directed assembly to insert targeted molecules into alkanethiolate self-assembled monolayers (SAMs) as the well-defined nanoscale environments in order to control their interactions and functions. The assembly strategies have been applied to molecules on both atomic-flat and curved surfaces. Surface-enhanced Raman spectroscopy (SERS), in combination with scanning tunneling microscopy, has been implemented as a powerful technique for studying the structures, interactions, dynamics, and reactions of these well-controlled molecules as individuals and in precise assemblies. In this talk, I present our recent progresses in applying directed assembly and SERS to study the nanoscale photophysics and photochemistry of three types of molecules isolated in alkanethiolate SAMs: the photoisomerization of azobenzene, the photo-isomerization of dihydroazulene, and the photoreaction of anthracene derivatives. The opportunities and challenges of employing flexible SERS substrates to further improve these studies will also be discussed.

“Gold nanofingers: a versatile platform for SERS sensing and imaging”

Steven Barcelo

SERS is a promising analytical technique for the detection of trace chemical and biological species. However, fabrication of low cost substrates capable of producing reliable and strong Raman enhancement, as required for the most interesting opportunities in trace detection and quantitative analysis, has proved challenging.

At HP Labs, we have developed a “nanofinger” platform capable of trapping analyte molecules in uniform, high intensity hot spots on a wafer scale. Nanofinger substrates consist of Au-coated flexible polymer pillars arranged to collapse into a designed assembly. Upon exposure to a volatile liquid and subsequent drying, microcapillary forces pull the pillars and their metal caps together into the designed structure, simultaneously trapping analyte molecules in the gap between adjacent particles. This process can additionally be used to fabricate deterministic nanoparticle assemblies which can then be transferred either onto a new substrate or into solution, allowing for new applications in sensing and Raman imaging. In this talk I will describe our work at HP Labs in developing this versatile platform, present a handheld spectrometer we have developed to enable mobile sensing and describe example applications in pesticide and food contamination sensing.

Gold-Plated Filter Membranes as a Platform for Surface-Enhanced Raman Spectroscopy

Jeremy Driskell

A novel surface-enhanced Raman spectroscopy (SERS) substrate has been developed via electroless deposition of gold onto filter membranes. The porous nature of this substrate is key to a recently developed SERS-based immunoassay that utilizes sample flow through the membrane to actively transport analyte to the sensing surface. Active transport overcomes diffusion limited binding kinetics that often impedes rapid analysis in conventional heterogeneous immunoassays and significantly reduces analysis time. Here we discuss the fabrication, characterization and application of this novel membrane. Electroless deposition of Au is controlled by plating time and SEM images demonstrate the reproducibility of the fabrication process. We then establish that the Au membrane can replace a rigid support as a viable capture substrate for a SERS-based immunoassay. It is demonstrated that an assay for mouse IgG is reduced from 24 h to 10 min and a 10-fold improvement in detection limit is achieved with the flow assay employing the Au membrane relative to the passive, i.e., no flow, assay.

Plasmonic Paper: An Emerging Analytical Platform for Trace Chemical and Biological Detection

Srikanth Singamaneni

Plasmonics involves the control of light at nanoscale using surface plasmons. One of the important manifestations of the confinement and control light at the nanoscale is the dramatic enhancement in the electromagnetic field at the surface of plasmonic nanostructures. This EM field enhancement at the surface of plasmonic nanostructures results in large enhancement of Raman scattering from molecules adsorbed on these nanostructures, which is often termed as surface enhanced Raman scattering (SERS). We will demonstrate how a common filter paper can be transformed into a plasmonic sensing platform for highly sensitive and selective detection of trace levels of chemical and biological analytes. Specifically, we will demonstrate how material - binding peptides can be transformed into a microfluidic paper-based analytical device (μPAD) using a simple lithography-free process by a simple cut and drop method. Apart from enabling rapid separation of complex analyte mixtures, this design generates a rapid capillary-driven flow capable of dragging liquid samples into a single cellulose microfiber, thereby providing an extremely pre-concentrated and optically active detection spot. Finally, a novel plasmonic calligraphy approach that enables multiplexed detection of chemical analytes is demonstrated using a simple ball-point pen as a deposition tool and functionalized gold nanorods as ink.

Flexible and UV-Cleanable SERS Substrates Based on Silver Nanoparticle Decorated Electrospun Nano-fibrous Membranes

Chaoyang Jiang

Porous electrospun nanofibrous membranes are excellent templates for preparing functional materials for a variety of applications such as catalysis and sensing. In this talk, I will present our recent work on the preparation, characterization, and SERS activity of silver nanoparticle decorated polymeric electrospun nanofibers. Two methods, chemical modification and oxygen plasma etching, will be used to modify the surface of polymer nanofibers for a better attachment of silver nanoparticles. Enhancement factors in the range of 105-106 were observed for those SERS substrates and the SERS signals were quite uniform with a relative standard deviation of ~10% across the overall sample. Anatase-phase titania nanofibers were utilized as the templating materials in order to obtain a UV-cleanable SERS substrates. Our work demonstrated a successful fabrication of SERS active electrospun nanofibers. With further optimization, such polymeric nanomaterials can be broadly applied in various SERS-based sensing applications.

Fabrication of SERS substrates using nanoparticle printing inks – role of thermal treatment in optimizing nanoparticle spacing.

Manuel Figueroa

There is a current demand to develop a low-cost, reliable process for fabricating reproducible SERS substrates with high amplification factors. Colloidal drop-deposited substrates are the simplest systems but suffer from a lack of stability and reproducibility. Signal intensities can vary widely across small target zones making it difficult to use for analytical measurements. An alternative is the use of nanoparticle inks which are encapsulated in a ligand shell that prevents aggregation in solution and upon printing. We show that commercially available nanoparticle inks can be used to fabricate reliable SERS substrates by applying a heat pre-treatment that partially removes the shell and reduces interparticle distances. Microwave absorption measurements are taken during heating to sensitively monitor nanoparticle spacing and find an optimal thermal treatment window for producing reliable SERS substrates. A relationship between microwave absorption and the SERS intensity is discussed. Furthermore, the substrate is shown to retain its morphology after adding a self- assembled monolayer of cysteamine for capturing larger molecules. In this presentation we discuss how the substrates can be used to study the conformational changes of such molecules.

Fabrication of Surface Enhanced Raman Scattering (SERS) Substrates using Nanoparticle Inks and Glass Fiber Fabrics

Som Tyagi

Although a variety of nano-lithographic methods have been employed with some success to fabricate SERS substrates, metallic colloids are still widely used due to the ease with which silver and gold nanoparticles can be produced. Nanoparticle inks are colloidal suspensions of silver or gold nanoparticles in water or some other suitable organic solvent. These nanoparticles can be sintered at relatively low temperatures (70 – 200^{o}C). We have shown that by controlling the sintering process SERS substrates containing fractal-like clusters can be obtained. Such substrates exhibit relatively high (108 – 109) SERS amplification factors (AFs). The high AFs in these clusters stem from a lack of translational symmetry that leads to localizations of electromagnetic excitations to very small regions that can create SERS hot spots. Recently, we have reported fabrication of flexible and porous SERS substrates obtained by depositing silver nano-particle inks on woven or spun fabrics made of glass fiber or cellulose followed by thermal annealing at 170 -2000^{o}C for 10 -15 minutes. Use of microwave absorption at about 10 GHz in the polymer-nanoparticle matrix to monitor the sintering process and to optimize the SERS amplification will also be discussed. By varying the annealing time, different levels of nanoparticle clustering and the consequent SERS amplification can be achieved. The 3-D intricate network of nanoparticle-decorated fibers leads to a large number of SERS hotspots that may result either from creation of optical nano-cavities or formation of particle clusters with varying sizes with favorable geometries. Sampling of large volumes using the SERS filter substrates to detect airborne molecules will be discussed.

Designer Plasmonic Antenna Architectures for Enhanced Spectroscopy

Jennifer S. Shumaker-Parry

Plasmonic nanoantennas manipulate light within nanoscale volumes based on structural properties. We use highly versatile approaches to produce plasmonic architectures with structural control in order to tailor the localized electromagnetic fields. Both colloidal metal nanoparticles and fabricated nanostructures serve as a basis for studies of the local field effects and the relationship to the structural details. Two approaches to creating the plasmonic antennas will be discussed. First, we localize surface ligands to induce assembly of noble metal nanoparticles in a controlled manner. The second approach makes use of the simple process of nanosphere template lithography to control structural details of fabricated plasmonic antennas. Localized photochemistry serves a dual purpose to map out the local fields of the nanostructures and to direct molecules of interest to surface regions to enhance spectroscopic signals. Challenges and opportunities related to the application of the designer plasmonic antenna architectures in chemical analysis and enhanced spectroscopy will be discussed.

Quantitative Bio-detection using SERS

Amanda J. Haes

A major limitation of nanosensors is irreproducible and/or changing surface functionality. Often, biological recognition elements in these sensors are composed of antibodies, functional groups, nucleic acids, etc. Because surface recognition layers can exhibit variability as a function of temperature, matrix, shelf life, and pH; surface chemistry and quality control measures that promote both nanomaterial stability and responsiveness are vital and motivate our investigations. In this presentation, the synthesis of standard optically-active, solution-phase noble metal nanostructures and their applications using localized surface plasmon resonance (LSPR) spectroscopy and surface enhanced Raman scattering (SERS) will be discussed for applications in the direct, qualitative and quantitative detection of small molecules with biological, chemical, and environmental applications. In the future, these results could be expanded for different nanomaterials cores, molecular targets, and sensor-based detection platforms.

Engineered SERS Substrates and Nanostructures

Sidney T. Malak,

Noble metal nanostructures have been combined with both planar and 3D substrates to fabricate a variety of SERS detection platforms. Porous alumina membranes (PAMs) act as an ideal substrate due to their high loading capacity for nanostructures, large light-matter interactions, flexibility, and flow-through capabilities. Nano-structures of different shapes (colloidal) can be deposited via vacuum infiltration or grown on the walls using an electroless deposition technique, allowing for a large amount of flexibility when designing the detection system. Electromagnetic modeling of nanostructures in the PAM shows large enhancement factors are possible. General control of the adsorption behavior (spacing) of nanostructures has been demonstrated and the resulting detection response has been investigated. More complex functionalization schemes of nanostructures using selective binding agents like aptamers are discussed with an aim for detecting stress related bio markers. This design allows for highly selective biotraps that would be appropriate for advanced selective, multiplexed detection platforms for larger analytes. Future systems would utilize aptamer-functionalized nanostructures with patterned, flexible substrates for selective detection.

Multi-layered SERS Substrates for Improved Third Dimensional Electric Field Enhancement

Pietro Strobbia

This talk will describe the development of a widely applicable multi-layered SERS substrate architecture/design capable of providing over two orders of magnitude enhancement in the enhancement factor of traditional SERS substrate geometries. This multi-layered architecture can be applied to a wide variety of SERS substrates and has been demonstrated to dramatically increase the electric field strength at the metal surface of the nanoparticles, by generating multiple oscillating plasmons that constructively interact with one another in the z-dimension. These multi-layered substrates are generated by applying alternating layers of metal (i.e. Au or Ag) and dielectric spacers. Early multi-layered substrates with alternating layers of silver/ silver oxide/silver, but having the same overall thickness, revealed further enhancements with each additional layer applied. Applying this alternating silver/silver oxide/silver geometry to various underlying roughened surfaces, significantly improved SERS enhancement factors were achieved, with idealized 2D patterned arrays fabricated with this multi-layered geometry providing SERS enhancement values as great as 1012 compared to spontaneous Raman. This talk will also discuss the characterization of this multilayered enhancement mechanism via various metal and dielectric spacer materials, and the fabrication of long lasting (non-silver based) SERS substrates with enhancement factors comparable to conventional silver versions of the same geometry.

Expanding the utility of SERS-based detection with chemical sensor molecules and porous, flexible SERS-active substrates.

Aaron D. Strickland

The molecular specificity provided by normal Raman scattering is a hallmark of vibrational spectroscopy and the reason for widespread use of Raman spectroscopy in analytical chemistry and the recent surge in commercial activity. Analytes having molecular structure that differs at one atom, such as benzenethiol and benzene thiolate, are easily differentiated by their unique Raman signature. While normal Raman scattering can be used to obtain significant information on molecular structure, typically only 1 Raman scattered photon is generated for every 108 photons incident on a given sample, which results in an insensitive analytical technique that is typically reserved for bulk materials. The solution to the insensitivity of normal Raman scattering was discovered in the late 1970's when researchers observed that molecules localized within a few nanometers of a roughened noble metal surface exhibited amplified Raman scattering on the order of 106 – 108; so-called surface-enhanced Raman Scattering (SERS). However, this 'limitation' can be used to ones advantages through appropriately designed interfacial chemistry. For this workshop, several SERS-active chemical sensors developed by iFyber researchers will be presented, showing how considerations in interfacial chemistry can impact the selective and sensitive detection of analytes using SERS. Examples will vary from the detection of metal ions, which lack a vibrational spectrum, to chemical nerve agents that do not effectively bind to SERS surfaces. In addition to these sensing techniques, we will also describe developments around several porous, flexible SERS-active substrate used to provide trace detection of a variety of analytes.

These substrates exhibit enhancement factors of >107, and are produced in large volumes with good substrate-to-substrate reproducibility (e.g., <15% relative standard deviation in measured signal). The substrates are used to effectively measure analytes of interest in solid, liquid and vapor phases using several different form factors that are not possible using standard wafer processed SERS substrates.

Large Area Flexible SERS Substrates based on Plasma Enhanced Atomic Layer Deposition of Ag

Orest Glembocki

Recently, it has been shown that Ag grown by atomic layer deposition (ALD) forms mosaic-like films with narrow (<5nm) cylindrically shaped gaps extending to the film base. The measured reflectivity has strong absorption in the visible region and the spectral position is thickness dependent in accordance with the cutoff frequency of coaxial spoof plasmonics. In addition, this form of Ag is also highly plasmonic with SERS enhances approaching 1E7. FDTD simulations replicate the reflectance spectra and show localization of electric fields in the gaps. Because the ALD process is conformal, we have succesfully been able to deposit SERS active ALD Ag on various types of substrates including, paper, fiber glass cloth, electrospun fibers, traditional solid substrates such as glass and Si and e-ebeam fabricated nanoparticles. The ALD process is compatible with for large areas and can enable large area flexible SERS substrates.