

POLITECNICO DI TORINO

MASTER THESIS IN NANOTECHNOLOGIES FOR ICTs

Lithography-free production of multiplexed anti-counterfeiting plasmonic security labels

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Declaration of Authorship

I, Adriano PITONI, declare that this thesis titled, "Lithography-free production of multiplexed anti-counterfeiting plasmonic security labels" and the work presented in it are my own. I confirm that:

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"Appare chiaramente che la cosa principale in cielo e in terra è obbedire per molto tempo e in una stessa direzione: a lungo andare ne risulta qualche cosa per cui vale la pena di vivere su questa terra, come per esempio, la virtù, l'arte, la danza, la musica, la ragione, lo spirito, qualche cosa che trasfiguri, qualche cosa di raffinato, di folle o di divino."

Friederich Nietzsche

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Abstract

Nanotechnologies for ICTs Dipartimento di scienze applicate DISAT in collaboration with Micro and Nanotechnology department at DTU (Denmark Technical University)

Master thesis

Lithography-free production of multiplexed anti-counterfeiting plasmonic security labels

by Adriano PITONI

The present work aims to fabricate anti-counterfeiting labels from a well developed SERS platform from the "Nanoprobes" group in the micro and nanotechnoogy department at DTU [1]. The latter device could lead to a very efficient platform for mass production purposes thanks to both of its low cost and low time high fabrication effectiveness. One of the key concept of this work is to explore the possibility of molecular spectra manipulation in order to create a very difficult fingeriprint that can be associated to any products or goods. Molecules metal multilayer encapsulation on top of the nanopillars SERS substrate is studied in order to overcome competitive binding and to achieve SERS spectra tuning regarding peaks relative intensities and map shapes as a first degree of security. A second technique of spectrum manipulation is studied using molecules mixture solution deposition. A final method is mentioned using molecules solution deposition by means of a nanoplotter in order to show the possibility of any pattern (e.g. letters, numbers, codes) on top of the SERS substrate.

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List of Abbreviations

SERS	Surface Enhanced Raman Spectroscopy
TERS	Tip Enhanced Raman Spectroscopy
SNOM	Scanning Near Field Microscopy
NPs	Nano Pillar s
PV	Photo Voltaic
RIE	Reactive Ion Etching
SEM	Scanning Eelectron Microscopy
SE	Secondary Electron
EM	Electro Magnetic
SPP	Surface Plasmon Polariton
LSP	Localized Surface Plasmon
LSPR	Localized Surface Plasmon Resonance
HOMO	Highest Ooccupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
PML	Perfectly Matched Layer
FEM	Finite Element Method
PPTT	Plasmonic Photo Thermal Thearpy
ICP	Inductively Coupled Plasma
BPE	trans-1-(2-pyridyl)-2-(4-pyridyl)-ethylene

Physical Constants

Speed of Light	$c = 2.99792458 \times 10^8\mathrm{ms^{-1}}$
Planck's constant	$h = 6.626 imes 10^{-34} { m J s}$
Mass of electron	$m_e = 0.911 imes 10^{-30} { m kg}$
Charge of electron	$e = 1.602 \times 10^{-19} \mathrm{C}$
Boltzmann's constant	$k_B = 1.3806 imes 10^{-23} \mathrm{J} \mathrm{K}^{-1}$
Vacuum permittivity constant	$\epsilon_0 = 8.854 imes 10^{-12} { m F} { m m}^{-1}$
Vacuum permeability constant	$\mu_0 = 1.256 imes 10^{-6} { m V} { m s} { m A}^{-1} { m kg}^{-1}$

List of Symbols

а	distance	m
P	power	$W (J s^{-1})$
t	time	S
Ε	electric field	$\mathrm{V}\mathrm{m}^{-1}$
Т	temperature	Κ
т	mass	kg
$\omega \text{ or } \nu$	frequency	Hz
$\omega \text{ or } \nu$	frequency polarizability	Hz $C m^2 V^{-1}$
$ \begin{array}{l} \omega \text{ or }\nu\\ \alpha\\ \epsilon\end{array} $	frequency polarizability dielectric function	Hz C m2 V-1 F m-1
$ \begin{array}{l} \omega \text{ or } \nu \\ \alpha \\ \epsilon \\ \sigma \end{array} $	frequency polarizability dielectric function cross section	Hz C m2 V-1 F m-1 m2
$ \begin{array}{l} \omega \text{ or } \nu \\ \alpha \\ \epsilon \\ \sigma \\ \lambda \end{array} $	frequency polarizability dielectric function cross section wavelength	$Hz C m^2 V^{-1} F m^{-1} m^2 m$
$ \begin{array}{c} \omega \text{ or } \nu \\ \alpha \\ \epsilon \\ \sigma \\ \lambda \\ \phi \end{array} $	frequency polarizability dielectric function cross section wavelength azimuthal angle	$Hz C m^2 V^{-1} F m^{-1} m^2 m rad$

Alla luce dell'ignoto. To the light of the unknown.

Chapter 1

Introduction

1.1 Motivation and scope

There is a strong need for novel anti-counterfeiting technology. According to the EU's agency for the protection of intellectual property (EUIPO), the EU loses €83 billion in sales and almost 800,000 jobs due to counterfeits and pirated goods. In Italy alone this accounts for losses of €7 billion and between 100,000 and 300,000 new jobs yearly.[2] Plasmonic security labels are emerging anti-counterfeiting platforms which can effectively encode multiple identification layers to deter forgery.[3] The building blocks of plasmonic security labels are plasmonic nano-antennas, i.e., nanostructures consisting of noble metals.[4] By tuning their composition, geometry and arrangement, a two-dimensional colour image can be generated at microscale to achieve the first anti-counterfeiting layer. Moreover, plasmonic nano-antennas have an exclusive feature - they can dramatically amplify the Raman scattering signals of molecules adsorbed on their surface. The effect is known as surface-enhanced Raman scattering (SERS). [5]Consequently, molecular information can be stored and encoded in plasmonic security labels. They can be read out exclusively by SERS imaging techniques. This leads to a Level 3 Security (L3S), meaning that information is not attainable unless the security label is decoded using forensic tools.[6]

Introducing the remarkable SERS effect and its basis principles the attention will focus on the on how this physical phenomenon can be used in one of the three main classes of SERS substrate: 1) metallic particles in colloidal solution; 2) 'planar' metallic structures, such as arrays of nanoparticles or pillars and 3) metallic electrodes. The first having usually the largest enhancement and cheapest production, but low signal reproducibility and reliability.[7]

As a matter of fact our analysis will focus on the application of a nanopillars (NPs) substrate, belonging to the second class. Thus starting from a very well developed SERS platform, with high performances, low fabrication cost and low fabrication time, during this thesis work it will be shown the possibility of creating a new SERS based anti-counterfeiting label having both a security level enhancement, as this novel labels aim to have, and a fabrication cost effectiveness in order to achieve mass production.

1.2 State of the art SERS labels

Several groups around the world have already attempted in the SERS platform application to anti-counterfeiting labels. Their works show micro meters resolution features obtaining good molecular spectra, by means of z-axis-dependency or by multiple metal layers encoding. Despite these high level results, they are mostly based on very complicated and expensive fabrication technique such as 2-photon lithography. Figure 1.1 shows the main results found in literature: images created by single point deposition of one or more than one different molecules. [3, 8, 9] For this reason using using the NPs device on which this work is based on could be extremely attractive for real world applications and commercialization. Mass production can be easily achieved for the low fabrication cost and time consumption. Especially by further study which could bring the metal cap coverage from the expensive noble metals (Au, Ag) to somenthing really cheap but still reliable in term of performances such as the aluminum.



FIGURE 1.1: State-of-the-art SERS labels from literature.[3, 8, 9]

1.3 Nanopillars (NPs) SERS platform

The whole thesis is based on one device: the NPs SERS platform. This device was invented by Michael Stenbæk Schmidt in the Nanoprobes group in micro and nanotechnology department at DTU in Denmark. The creation of a silicon "nano grass" substrate successively covered by metal caps, allows the SERS effect in order to exploit an enhancement of Raman effect. This platform has several application in bionanotechnology, essentially based on spectroscopic analysis of bio-analytes such as antibiotics residues in food products [10], biomolecules detection in low concentration [11] or anti terroristic chemicals (nerve gas) detection [12] biomarkers detection [13] and microbials quantification [14]. The latter are only few of the many applications SERS spectroscopy and our NPs platform have. The working principle fo our device (figure 1.1) relies on the analyte trapping inside electromagnetic hotspots created by NPs leaning among each others. Thanks to this bending feature NPs exploit basically two mechanisms in order to activate the SERS effect and improve analytes detection for Raman spectroscopy:

- electromagnetic hotspots: plasmonic resonance needed for SERS is achieved among several clusterizing NPs;
- trapping: the leaning effect literally is used for letting analytes sitting on the NPs surface;



FIGURE 1.2: NPs SERS device working principle.[10]

1.4 SERS applications

As previously mentioned SERS applications range within a large area from bionanotechnologies to material sciences, but especially in life science. In this section we give a closer look to some interesting applications. Figure 1.3 shows one application using the NPs substrate also present in this work. Here NPs gold caps are functionalized by means of sepcific aptamers for quantitative detection of TAMRA labeled vasopressin (TVP) in the pico-molar range (1 pM - 1 nM). Both specific NPs functionalization and concentration dependant signal are analyzed in this work showing the possibility of ultra sensitive and specific detection of biomolecules in the pico-molar range. Aptamer are strongly immobilized on NPs caps using the high binding covalent strength of thiols with gold. After that the TVP sample is introduced for a certain incubation time and temperature. Then all non specifically bound molecules are washed away and finally the leaned NPs can be exposed to Raman measurements exploiting the high signal amplification inside hotspots. [15]

Figure 1.4 shows other several configuration where SERS effect can be used. In (a) gold nanoparticles are fixed onto a substrate whereas in other applications nanoparticle can also be found suspended in solution instead of being stucked on solid surface. In general nanoparticles in solution are easy to produce, but more affected by fluctuation in order if some reproducibility and reliability are needed. (b) shows another way of nanoparticle implementation using a first transition metal core particle and then a coverage of gold on the surface. In (c) there is one of the



FIGURE 1.3: The NPs structure can be functionalized for biomolecules highly specific detection. Firstly aptamers are immobilized on NPs cap and then incubated with TAMRA vasopressin.[15]

most promising and already implemented way of single molecule detection that is TERS which means tip enhanced raman microscopy. In this approach the analytes can be found on any type of substrate and the enhancing effect is exploited only through the sample-tip region. The last picture represents the SHINERS (shellisolated nanoparticle-enhanced Raman spectroscopy) approach presented in [16]. These SHINERS are a matrix of gold nanoparticles covered by an ultrathin layer of silica or alumina in order to prevent nanoparticles agglomeration, preventing a direct contact with sample analytes and allowing nanoparticles to be adapted on several kind of substrates.



FIGURE 1.4: SERS can be exploited using different type of substrate for analytes detection: (a) gold nanoparticles array; (b) transition metal nanoparticles covered by a gold layer on the surface; (c) TERS and (d) SHINERS.[16]

1.5 Chapters summary

- **CHAPTER 2**: the theoretical background section is devoted to the introduction on the basis of the two main field constituting SERS, that is Raman spectroscopy and plasmonics. Starting from the basis of electromagnetism it is possible to describe the phenomena under the power of SERS;
- **CHAPTER 3**: COMSOL multiphysics software can be used in order simulate the EM wave NPs nanostructure interaction using a simple model;
- **CHAPTER 4**: the main fabrication techniques used for the NPs creation are introduced from a theoretical point of view. Afterwards the proces steps are described. Finally an overview on the equipment used during the work is done;
- **CHAPTER 5**: structure characterization performed by SEM is of key importance in order to understand the morphology of the substrate used for Raman microscopy. The basis of SEM theory is introduced and the main feature of an electron microscope are described, highlighting the peculiar aspects of NPs characterization. SEM pictures of NPs are shown. Finally Raman microscope tool and its working principles are described.
- **CHAPTER 6**: the main section describes results obtained thanks to the NPs properties. Firstly a multiple metal layers structure strategy is implemented in order to overcome competitive binding and let several molecules of different composition and Raman section sit together on the same NPs sample. A second strategy using direct deposition of mixed molecules solution is described. The latter alowing a faster and easier deposition, including the possibility of overcoming competitive binding and also adding the spot map shape of the deposited drop as a tunable parameters. Finally a third method shows the usage of a nano dispenser tool is shown in order to create pattern starting from the analyte solution;
- CHAPTER 7: future perspectives and improvements are discussed in this section. The promising results of this work would suggest a further study reling on cheaper material implementation and polymer based incapsulation in order to create a mass-producible and cost efficient platform with good performances an high durability.

Chapter 2

Theoretical background

Surface enhanced Raman scattering is a physic-chemical effect exploiting which a very high signal enlargement can be taken from the Raman spectroscopy technique. Signal amplification effect comes electromagnetically from plasmon resonance within metal nanostructure and chemically thanks to adsorbed molecules on the surface. SERS is a phenomenon firstly observed in 1973 and the single molecule detection (1997 [17]) obtained thanks to it, attracted a lot of increasing interest into this technique, whose high molecular specificity coming from the Raman effect combined together with a good signal intensity and sensitivity demonstrated that this technique could have rivaled with fluorescence analysis. Since than SERS was widely studied in many multidisciplinary approaches and in many different fields of application.

Describing SERS requires information from many different fields such as electromagnetic wave - matter interaction and quantum chemistry. In this section the basis concepts of SERS technique starting from Raman spectroscopy and its principles. Afterwards an introduction on plasmonics will follows. Combining the knowledge coming from both these field, an overview on SERS can be achieved. Raman spectroscopy and thus SERS application range from semiconductor and in general solid state characterization to nanobiotechnology and health science. The following theretial review will focus more on the molecules and chemistry applications based on Raman and SERS, overlooking the solid state considerations needed to explain the interaction with photons with the ordered lattice of a crystalline structure.



FIGURE 2.1: Artistic representation of a LSPR mode enchancing the EM field at Au nanoparticles surface.

2.1 Raman spectroscopy

Raman scattering was discovered by sir C.V. Raman, an indian physicist, and is a powerful scattering technique use for the analysis of the internal structure of molecules and crystals and also for sensing purpose. Raman effect it can be defined as the anelastic scattering of light. Directing a monochromatic light beam on to a sample, the scattered light from it can be detected and analysed in terms of frequency and polarization. Most of the scattered light will have the same signal of the impinging photons, whereas a small amount of it will be frequency shifted with respect to the incident excitation wavelength. Therefore Raman spectroscopy measures the amount of scattered light, which is correlated to molecular vibrational motions. Many different spectroscopic techniques can be implemented in science each one having signal coming from a different physical phenomenon. For example another spectroscopy technique based on vibrational motions of molecules is the infrared (IR) spectroscopy, which is based on the photons absorption and not on the light scattering. IR is a complementary spectroscopic technique for vibrational states of a molecule. Raman spectroscopy has to be distinguished also from fluorescence (and phosphorescence) one where a photon is released by an excited molecule going into a ground state. The latter are not exactly scattering process because they are involving a two steps (absorption and spontaneous emission) process whereas a proper scattering event is instantaneous, that is a photon absorption and emission occurs at the same time. In fact both fluorescence and phosphorescence are characterized by relaxation times. Another important difference between Raman scattering and fluo(phospho)rescence is that during Raman scattering the excited electron doesn't need a real excited state, thus it gains energy reaching a virtual energy state. Fluorescence signal is higher than Raman one because the latter involves low probable inelastic events whereas the former involves higher energy in its occurency. Therefore many times fluorescence can be a problem for Raman spectroscopy disturbing its signal, but this is the case using low wavelength laser, going to UV regime. That's not the case of this work, so that fluorescent events will be neglected.



FIGURE 2.2: Many signals involved in Raman spectroscopy related to different physical phenomena.

The term "scattered" light refers to an induced-dipole creation which will emit light as a consequence of the impinging beam. This phenomenon requires a semiclassical description of the electromagnetic radiation - matter interaction. The electron cloud of a molecule is distorted under the presence of an harmonic electromagnetic external perturbation $E = E_0 \cos(2\pi v t)$. The electrons periodic oscillation occurs at the same frequency v_o of the incoming field creating an induced dipole moment $P = \alpha E$ which results in a secondary electromagnetic radiation source, that is the scattered light. The term α is the molecule polarizability and has a fundamental role in the Raman effect. It describes the grade of deformability inducable in a molecular orbital. The atoms displacement around their equilibrium position Q_0 is $dQ = Q_0 \cos(2\pi v_{vib}t)$ where vvib is the frequency of the vibrational mode involved in the transition. The polarizability is changing as the molecule vibrates thus since a typical dipolar molecule undergoes small vibrations, α can be approximated by a Taylor expansion:

$$\alpha = \alpha_0 + \frac{\partial \alpha}{\partial Q} dQ \tag{2.1}$$

Where α_0 is the polarizability of the molecular mode at the equilibrium position. Using the latter equation combined with the dQ expression plus the previous definition and some trigonometric identity, the dipole momentum can be written as:

$$P = \underbrace{\alpha_0 E_0 \cos(2\pi\nu_o t)}_{\text{Rayleigh}} + \frac{1}{2} Q_0 E_0 \left(\frac{\partial \alpha}{\partial Q}\right) \underbrace{\left\{ \cos[2\pi(\nu_o - \nu_{vib})t] \right\}}_{\text{Stokes}} + \underbrace{\cos[2\pi(\nu_o + \nu_{vib})t]}_{\text{Anti-Stokes}}$$
(2.2)

First of all the linear dependency within the incident field is observed. Then looking at the latter equation the main events involved in Raman spectroscopy can be higlighted and also the fundamental selection rule (always talking from a classical point of view) can be extrapolated. In the dipole momentum expression three terms can be easily distinguished belonging to three different frequency: the first term corresponding to Rayleigh scattering, that is elastic scattering having the same frequency of the incident excitation occuring most likely whereas the other two terms inside curly brackets belong to inelastic scattering indeed at down-shifted frequency ($\nu_o - \nu_{vib}$) called Stokes events and up-shifted frequency($\nu_o + \nu_{vib}$) for anti-Stokes ones. After this scattering classification the second important thing as to be observed, that is anelastic scattering only occurs if:

$$\left(\frac{\partial \alpha}{\partial Q}\right) \neq 0 \tag{2.3}$$

Therefore the condition in order to have Raman scattering is that the molecule has to change its polarizability during vibration.

Another useful expression according to classical electromagnetism is the radiation intensity emitted by an oscillating dipole: $I = \frac{v_o^4}{12\pi\epsilon_0 c^3} |p^2|$. By substitution in equation 2.2:

$$I = \alpha_0^2 E_0^2 \cos^2(2\pi\nu_o t) + \frac{1}{2} Q_0^2 E_0^2 \left(\frac{\partial \alpha}{\partial Q}\right) \{(\nu_o - \nu_{vib})^4 \cos^2[2\pi(\nu_o - \nu_{vib})t] + (\nu_o + \nu_{vib})^4 \cos^2[2\pi(\nu_o + \nu_{vib})t]\}$$
(2.4)

The power fourth frequency and field squared dependencies can be obtained and also the need of a more detailed model arises. In fact by comparing stokes and anti-stokes intensities in this classical fashion, it would be an identical presence of the two events, which is not true experimentally.

Therefore the simple semi-classical picture can be satisfactory in order to describe the Raman effect in its most general aspect. But of course a quantum mechanic picture is needed in order to have a complete understanding of every aspect involved in such phenomenon and to be able of making distinction among other radiative events. First of all the quantum view gives us a picture maybe simpler to visualize the process. As it can be seen in figure 2.2 the Raman scattering process can be explained by means of energy levels structure picture by splitting the process into the events, even though we have already said that is not a multistep process. Thus the incoming photon gives energy to conduction electron which will reach a so called virtual state. Afterwards the electron will decay in an higher energy level (if its starting point is the ground state) or to the ground state. The former case describes the Stokes event whereas the latter describes the anti-Stokes event. The virtual state has such a name because is not a stationary state and is not a Schrödinger equation solution and does not correspond to a well defined energy level. The anti-Stoke is less probable event because the initial electronic state should be an already excited state. Therefore in this quantum mechanical model the scattering intensity depends on the occupation of the initial state, which is determined by the Boltzmann distribution. Hence according to the Boltzmann distribution it is possible to explain why anti-Stokes events are less probable and their peak is negligible respect to Stokes event:

$$\frac{I(Stokes)}{I(anti-Stokes)} = \frac{(\nu_o - \nu_{vib})^4}{(\nu_o + \nu_{vib})^4} e^{(h\nu_{vib})/k_BT}$$
(2.5)

Moreover thanks to quantum mechanics it can be easier understandable why Stokes events are more probable than anti-Stokes and consequently why Stokes peaks signal is stronger than anti-Stokes ones.

Another step into a deeper understanding of the Raman event coming from quanto mechanics consideration involves the scattering cross section, but this will explained at the beginning of chapter 6.



FIGURE 2.3: Raman scattering process of EM wave impinging on a molecule and the very low fraction of anelastic (Raman) signal respect to elastic (Rayleigh) one.[18]
Raman technique is a very powerful spectroscopic technique, but has a huge disadvantage: the signal coming from anelastic scattering is very weak. The intrinsic nature of anelastic scattering is based on poorly probable events. As a mater of fact an incoming photon interacting with one atom, it can interacts with its electron cloud or its nucleus. The probability for one photon to interact with electrons of one atom is much higher than the one describing the interaction of this photon with its nucleus. The interaction of photons with electrons do not result in a significant scattering of photon energy: this corresponds to the Rayleigh process. On the other hand, while interacting with nucleus, the photon exchange a significant amount of its energy: this is the Raman process. Therefore since Raman event accounts for something occurring with low probability thus the signal coming from this effect is very low. That's the reason why signal enchancement is needed. Thanks to plasmonic nanostructure, Raman signal can be amplified and here is where SERS comes from. [7]



FIGURE 2.4: Raman spectroscopy energy levels transition picture: (a) Rayleight scattering; (b) Stokes scattering; (c) anti-Stokes scattering.[18]

2.2 Plasmonics

The electromagnetic enhancement used by SERS is based on the localized surface plasmon resonance (LSPR) concept from plasmonics. The latter science field definition comes out bringing together plasma and electrons. Delocalized (free) electrons in a metal can be resonantly excited by an external electromagnetic force (e.g. laser). The word "plasma" is used in this solid state environment in analogy with a gas plasma: free electrons of a metal move in a fixed lattice of positive charges, giving rise to the so called free-electron plasma or solid state plasma. When a metal structure having a smaller size than the incoming wavelength (sub-wavelength) is excited by an electromagnetic force which leads to an induced dipole emitting at the same exciting frequency (close to the plasma resonance frequency) but at higher field intensity. (resonant elastic scattering from a metal structure). The latter is the basic concept above the electromagnetic enhancement exploited by SERS.

In order to introduce the concept of plasmon it is needed to begin talking about some basic quantities. Starting from Maxwell's equations it is possible to describe the electromagnetic field with metal in the classical fashion:

$$\nabla \cdot \mathbf{D} = \rho \tag{2.6}$$

$$\nabla \cdot \mathbf{B} = 0 \tag{2.7}$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \tag{2.8}$$

$$\nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \tag{2.9}$$

Where **D** corresponds to the dielectric displacement, **E** to the electric field, **H** to the magnetic field and **B** to the magnetic induction. The latter macroscopic physical quantities are then connected to the external charge density ρ and current density J. The additional constitutive material dependent relations have to be considered:

$$\mathbf{D} = \epsilon_0 \epsilon \mathbf{E} \tag{2.10}$$

$$\mathbf{B} = \mu_0 \mathbf{H} \tag{2.11}$$

Where the frequency dependent dielectric constant $\epsilon = \epsilon(\omega)$ is a key parameters we are going to analyze deeper in the following and it is in general a complex fucntion $\epsilon = \epsilon' + i\epsilon''$. The latter being connected with the complex refraction index by $n = n + ik = \sqrt{\epsilon}$. The following expression account for explicit dependency:

$$\epsilon' = n^2 - k^2; \qquad \epsilon'' = 2nk \tag{2.12}$$

$$n^{2} = \frac{\epsilon'}{2} + \frac{1}{2}\sqrt{\epsilon'^{2} + \epsilon''^{2}}; \qquad k = \frac{\epsilon''}{2n}$$
(2.13)

The ϵ real part describes the dispersion and polarization in the medium, whereas the imaginary part is connected to absorption. After this breafly introduction, the electron gas Drude model will lead us to the plasmon definition [19]. Afterwards distinctions among many different types will bring us to our plasmon type of intereset, that is the localized plasmon, exploiting which the electromagnetic surface

enhancement effect can be used for SERS. [7, 19, 20]

The plasma model depicted from Drude describes an electron gas of density N propagating behind a background of positive ions. Exciting this electron gas (having effective mass m) with an EM field $\mathbf{E}(t) = \mathbf{E}_0 exp(-i\omega t)$ and considering a damping effect with a characteristic rate $\gamma = 1/\gamma$ the following equation of motion can be considered (neglecting the restoring force):

$$m\ddot{x} + m\gamma\dot{x} = -e\mathbf{E}(t) \tag{2.14}$$

having the solution

$$x(t) = \frac{e}{m(\omega^2 + i\gamma\omega)}\mathbf{E}(t)$$
(2.15)

The electrons displacement generates a polarization $\mathbf{P} = -Nex$ leading to the frequency dependent dielectric constant definition:

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} = \epsilon_0 \epsilon \mathbf{E} \tag{2.16}$$

$$=\epsilon_0 \left(1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}\right) \mathbf{E}$$
(2.17)

$$\Rightarrow \epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} = 1 - \frac{\omega_p^2 \tau^2}{\omega^2 \tau^2 + i\omega\tau}$$
(2.18)

where the plasmon frequency has been introduced $\omega_p^2 = Ne^2/(\epsilon_0 m)$. For high frequency approximation $\omega \tau \gg 1$ the damping term vanishes and $\epsilon(\omega)$ becomes approximately real:

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \tag{2.19}$$

Whereas the dispersion relation of the EM field can be found from $k^2 = |\mathbf{k}^2| = \epsilon \omega^2 / c^2$:

$$\omega(k) = \sqrt{\omega_p^2 + k^2/c^2} \tag{2.20}$$



FIGURE 2.5: Dispersion relation of the free conduction electron gas from the Drude's plasma model.[19]

Figure 2.4 shows the dispersion relation behavior: no propagation of EM waves below plasmon frequency $\omega < \omega_p$ whereas for $\omega > \omega_p$ waves propagate at a group velocity $v_g = d\omega/dk < c$. It is straightforward to notice that for $\omega = \omega_p$ thus $\epsilon = 0$.

The collective oscillation of the conduction electron gas respect to their positive ions environment can be described either as a collective longitudinal excitation mode $(\mathbf{k}||\mathbf{E})$ either as the quanta of this charge oscillation called plasmon. Specifically this description corresponds to bulk-plasmons, which has to be differentiated respect to surface-plasmon. As a matter of fact the former cannot couple to transversal EM fields and cannote be excited by direct irradiation, because of their purely longitudinal nature. The specific plasmon type useful for SERS, that is the localized surface plasmon (LSP), belongs to the family of surface-plasmon. Before that we should introduce surface plasmons.



FIGURE 2.6: Dielectric-metal interface where SPP can propagate.

Surface plasmons or more precisely surface plasmon polaritons (SPP) are EM excitations propagating at the interface between two materials having opposite signs dielectric functions, in general dielectric and metal. Starting from the Helmoltz equation, which is the harmonic field wave equation:

$$\nabla^2 \mathbf{E} + k_0^2 \boldsymbol{\epsilon} \mathbf{E} = 0 \tag{2.21}$$

Where $k_0 = \frac{\omega}{c}$ is the wave vector in vacuum, the electromagnetic modes analysis can be done at the dielectric-metal interface like in figure 2.5. Therefore we have $\epsilon = \epsilon(z)$ and the EM wave propagating along x-direction $E(x, y, z) = E(z)e^{i\beta x}$ at z = 0. Where $\beta = k_x$ is the complex propagating constant and

$$E(z) = E_0 e^{k_z z} = E_0 e^{ik'_z z} e^{-k''_z z}$$
(2.22)

Where $k_z = k'_z + ik'_z$ is the complex wave vector along the direction perpendicular the materials interface. These two parameters β and k_z will be of fundamental importance to define the surface plasmons existance condition. The E(x, y, z) expression in 2.21 leads to the wave equation:

$$\frac{\partial^2 \mathbf{E}(z)}{\partial z^2} + (k_0^2 \epsilon - \beta^2) \mathbf{E} = 0$$
(2.23)

Which is the equation governing the guided modes into waveguides. Therefore surface plasmons can be considered EM modes, just like in waveguides.

Finding all the electric and magnetic field components in the two regions and imposing the continuity condition of $\epsilon_i E_z$ and $E_{i,x}$ at the interface, the propagating wave solution confined to the interface, i.e. having evanescent (exponential) decay in z-direction, implies the following condition [21]:

$$\frac{k_2}{k_1} = -\frac{\epsilon_2}{\epsilon_1} \tag{2.24}$$

Finally the $H_{i,y}$ components have to fulfill the wave equation 2.23 ($H_{i,y}$ instead of E): $k_{1,z}^2 + k_0^2 \epsilon_1 - \beta^2 = 0$ and $k_{2,z}^2 + k_0^2 \epsilon_2 - \beta^2 = 0$ leading to the dispersion relations valid for both real and imaginary ϵ :

$$\beta = k_0 \sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}} \tag{2.25}$$

$$k_{i,z} = k_0 \sqrt{\frac{\epsilon_i^2}{\epsilon_1 + \epsilon_2}}; \qquad i = 1, 2$$

$$(2.26)$$

Finally we obtain the conditions in order to have a confined EM wave with exponential decay in the direction perpendicular to propagation and a propagating mode along x-direction. The first condition implies that both materials have $k_{i,z}$ purely imaginary in order to have $E(z) = e^{-k_z^{-2}z}$ that is we need $\epsilon_1 + \epsilon_2 < 0$ from 2.26. Whereas the second condition implies that the propagation constant is purely real, which leads to $\epsilon_1 \epsilon_2$ and $\epsilon_1 + \epsilon_2$ both positive or negative from 2.25. Therefore in order to satisfy this conditions we need materials of dielectric function having opposite signs and one ϵ larger than the other. This is the explanation why metals, having $Re(\epsilon) < 0$ (figure2.6), dielectric interface presents surface plasmon polaritons.



FIGURE 2.7: Dispersion relation of surface plasmon compared to light propagation in vacuum and into dielectric.

Figure 2.6 shows the disperion relation of surface plasmons according to 2.25 equation. For small k values β is close to k_0 and the light line, that is propagation in vacuum. For large k values 2.18 can be insert into 2.25 having the surface plasmon frequency:

$$\omega_{sp} = \frac{\omega_p}{\sqrt{1 + \epsilon_{dielectric}}} \tag{2.27}$$

Which leads to the $\omega_{sp} \approx \omega_p / \sqrt{2}$ value correspondings to $\epsilon = -\epsilon_{dielectric}$. In this regime the velocity group goes to zero thus in this condition the mode is non propagating and it can be called surface plasmon (without polaritons). The last plasmon

type is the one used in SERS application and it is the localized surface plasmon. This is still a surface plasmon polariton itself but it is non propagating and occurs on conductive nanostructures having the size smaller or comparable to the exciting wavelength. The first example in order to show this plasmon type is the nanoparticle inside an EM oscillating field. Its curved shaped surface excerts a rstoring force on electrons, given rise to resonance, leading to EM field enhancement. Another difference with the propagating surface plasmon is that it can be activated by direct illumination, without phase matching need for surface plasmon activation. LSP modes belong to metallic nanostructure, therefore there is no need to fulfill the previous metal-dielectric conditions, even though resonance condition is still linked to a negative real part of ϵ . The resonance for gold and silver nanoparticles occurs into the visible region of the EM spectrum. Another important characteristic is the geometry dependency: small conductive object resonance is not instrinsically related to the material property but also to shape. Two objects made by the same material can have different resonances depending on their geometry.



FIGURE 2.8: Real (A) and imaginary (B) part of Au (gold) and Ag (silver) dielectric function with respect to wavelength from Jhonson and Christy. [22]

Already used Drude's model needs it was a simplified version, whose validity vanishes between near-infrared and visible. The complete model introduces restoring force coming from bound electrons. This improvement is fundamental both for the LSP and gold and silver visibile properties description. In order to account for interband transitions 2.14 can be modified with an additional restoring term:

$$m\ddot{x} + m\gamma\dot{x} + m\omega_0^2 x = -e\mathbf{E}(t) \tag{2.28}$$

Which leads to a more complete expression for the dielectric function:

$$\epsilon(\omega) = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega}$$
(2.29)

Being ω_0 the bound electrons resonance frequency. Hence now the complete model takes into account longitudinal electron oscillations and interbands transitions occuring in gold. Including bound electrons can be used also to justify the noble metal high reflectivity in the visible range. Gold and silver are the most widely used material for many reasons:

- plasmon resonance in the visible range (usually metals have plasma frequency in the UV range): visible wavelength lasers can be used;
- negative $Re(\epsilon)$ as fundamental requirement for plasmonic applications;
- low *Im*(ε): which corresponds to low absorption in the visible range, corresponding to low losses and thus a greater EM enhancement for Ag than for Au. On its advantage, Au exhibits higher oxidation-stability and bio-compatibility;

The final step of this theoretical section is focused on the analysis of the EM enhancement effect coming from LSP resonance. In order to do so it is usefule to present the spherical nanoparticle example. Using the quasi-static approximation, a particle of size $d \ll \lambda$ (i.e. d below 100 nm) inside an harmonically oscillating EM field feels the field as almost constant over its volume so that the field can be considered electrostatic. The timen dependence can be added in a second moment. In this electrostatic approach the aim is to find the electric field $\mathbf{E} = -\nabla \Phi$ using the Laplace equation $\nabla^2 \Phi = 0$. Following the computation in [19] the final important results is the complex polarizability:

$$\alpha = 4\pi a^3 \frac{\epsilon(\omega) - \epsilon_m}{\epsilon(\omega) + 2\epsilon_m}$$
(2.30)

Being the Clausius-Mossotti like form. Where a is the particle radius and ϵ_m is the dielectric constant of the surrounding medium and ϵ is the complex dielectric function belonging to the metal particle. Having a resonant enhancement at $|\epsilon = 2\epsilon_m|$ which in case of slowly varying $Im(\epsilon)$ around resonance frequency, becomes

$$Re[\epsilon(\omega)] = -2\epsilon_m \tag{2.31}$$

That is the so called Fröhlich condition associated to the dipole surface plasmon mode. For a a sphere made by a Drude metal with epsilon as the one described in 2.18 it can be obtained $\omega_{LSP} = \omega_p / \sqrt{3}$. Finally the electric field enhancement can be described by means of

$$\mathbf{E}_{sca} = \frac{3\epsilon_m}{\epsilon(\omega) + 2\epsilon_m} \mathbf{E}_{in}$$
(2.32)

The latter equation helps to explain the EM enhancement coming from spherelike sub-wavelength nanostructure essential for SERS application. Using a metal whose electric constant is negative, the Fröhlich can be satisfied, achievieng an incredible scattered electric field coming from the sphere. Both $Re(\epsilon)$ and $Im(\epsilon)$ play an important role: the first isnure the resonance condition; whereas the second quantifies the amplification effect, due to internal losses from absorption.

In order to characterize this kind of nanostructure, the scattering cross sections have to be defined. These quantities help to define not only to their resonance peak but also to understand nanostructures behavior as a function of their geometry, shape, size, material and surrounding environment (figure 2.8). Thus from the oscillating dipole radiated power ($P = \omega^4/(12\pi\epsilon_0\epsilon_m c^3)|\mathbf{p}|^2$) divided by the intensity of the incoming EM wave ($I = (1/2)c\epsilon_0\epsilon_m E_0^2$):

$$\sigma_{sc} = \frac{k^4}{6\pi\epsilon_0^2} |\alpha(\omega)|^2 = \frac{8\pi}{3} k^4 a^6 \left| \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \right|^2$$
(2.33)

Power from incident light is not only due scattering but also to absorption. Thus in general it is defined an extinction cross section $\sigma_{ex} = \sigma_{sc} + \sigma_{abs}$. Using the Poyinting's vector theorem, the absorption cross section for a metallic sub-wavelength sphere is:

$$\sigma_{abs} = \frac{k}{\epsilon_0} Im(\alpha(\omega)) = 4\pi k a^3 Im\left(\frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m}\right)$$
(2.34)



FIGURE 2.9: (A) σ_{sc} for Au and Ag in vacuum (solid), water (dashed) and glass (dash-dotted) [23]; (B) Ag capped NPs scattering spectra measured with dark-field microscopy at different Ag thicknesses before and after NPs leaning. [24]

Finally the EM enhancement can be expressed using two contributions: the local field enchancement coming from the excitation power and the radiation enhancement due to the re-emission, expressed by the already mentioned oscillating dipolar power emission. Therefore the classic SERS EM enhancement factor is:

$$I_{SERS} = I_{inc}(\omega_{inc})I(\omega_{inc} - \omega_{vib}) = |E_{inc}(\omega_{inc})|^2 |E(\omega_{inc} - \omega_{vib})|^2$$
(2.35)

Usually the difference between the incoming light and the scattered light frequency is negligible respect to the LSP mode linewidth. Thus the usual expression is $I_{SERS} \approx |E(\omega_{inc})|^4$.

Plasmons summary can be helpful to have a general look over the wide field of plasmonic applciations:

- bulk(volume)-plasmon: quantum of electron gas collective oscillation inside in a metal-like medium propagating through the volume for *ω* > *ω_v*;
- surface plasmon polariton (SPP): evanescent (in direction perpendicular to the interface) electromagnetic wave propagating at the interface between two opposite dielectric function material (i.e. metal-dielectric). Analogy with with propagating TM modes in a dielectric waveguide;
- localized surface plasmon polaritons (LSP): localized mode (non propagating in all directions: evanescently exponential decay) which can be exploited for electro-magnetic field amplification;

2.3 Electromagnetic and chemical enhancement

Summarizing all the effect involved in the previous disquisition on SERS we end up with a general expression dependency of the power coming from EM aspects of SERS analysis [25]:

$$P_{SERS} \propto N I_L |A(\omega_L)|^2 |A(\omega_S)|^2 \sigma_{ads}^R$$
(2.36)

Where: N is the number of molecules involved in the process; I_L is the laser intensity; σ_{ads}^R is the Raman cross section of the analyte adsorbed on the SERS substrate (it will clarified in section 6); $|A(\omega_L)|^2$ and $|A(\omega_S)|^2$ are the enhancement factors coming from the excitation and the scattered fields.

After reasoning about the EM enhancement effect, a brief discussion about the second enhancement effect involved in SERS has to be done. Plasmonic resonance could exists without an adsorbate analyte molecule on the metal nanostructure, but one of the main purpose of SERS is bio-sensing, that is very low concentration detection of bio-molecules in liquid solution or even in gaseous environment (even simple detection in air). Once the molecule (or molecules cluster) bonds to the metallic structure several effects take place contributing to the amplification of the outcoming EM signal from the sample surface. The exact description of the mechanism is still object of studying, but the main processes involved are: the change of polarizability of the adsorbate molecule inducing resonant-Raman scattering and the most widely accepted description involvind the charge transfer between electronic levels of the metal-analyte conjugate. [26, 7] In this description seems to be easy to understand that oppositely to the EM enhancement, the CE (chemical enhancement) depends on the type of analyte and on its relation with the specific metal structure. Despite its complexity, the CE is a weaker effect respect to the EM enhancement, whose is the main responsible for SERS success.



FIGURE 2.10: Representation of the charge transfer mechanism between metal-analyte energy levels. (a) when the laser energy is in resonance with a metal-molecule conjugate transition; (b) and (c) if there is an indirect coupling between metal and analyte.[7]

The already mentioned virtual state needed for the Raman transition can lies directly withint the molecular levels. The formation of this molecule-metal complex could lead to an energetic gain (due possibly to surface energy state on the metal) giving the possibility to an electron in the molecule to be excited overcoming the HOMO-LUMO gap. Transition otherwise impossible with the simple laser excitation.

The most important actore in the Raman signal amplification purpose is for sure the EM one, reaching $10^8 - 10^{11}$ values. Whereas the CE factor reaches at its maximum efficiency values of 10^2 . Summarizing both enhancement factor it can be said that : $EF_{tot} = EF_{EM} \cdot EF_{CM}$ leading to a maximum reachable valuable of around 10^{14} , allowing the single molecule detection.

2.4 Plasmonic applications

Plasmonic features find applications not only in SERS and TERS but in many others fields such as optoelectronic elements, photovoltaic cells and cancer treatment or biomedical in general. In figure 2.11 it can be seen several subwavelength waveguide components operating at telecom wavelengths: Y-splitters and Mach–Zehnder interferometers. The hybrid nature of plasmonic components takes advantage from the superior operational bandwidth of photonic elements, but are not confined by the diffraction limit thanks to subwavelength metal structure. This plasmonic components can be applied into bio-sensors miniaturization and for ultra compact interconnection that can be easily integrated with electronic circuits.



FIGURE 2.11: Plasmonic Y-splitter and Mach-Zehnder (MZ) interferometer SEM (a), topographical (b) and SNOM (c) images from [27].

The second plasmonic application example is in the field of photovoltaic (PV). Figure 2.12 shows different strategies in order to implement efficiently plasmonic nanostructures in order to enhance the harvested current. Such structures may be helpful to overcome the main problems limitating PV future development. As a matter of fact the reduced acceptance angle of the active region and the limited spectral sensitivity of the active material could be improved thanks to plasmonic using light trapping schemes (figure 2.12) which concetrate light in the active region doing this in a specific spectral region where the active material has maximum absoprtion. The future steps are based on using hybrid metal and low-losses and high permittivity dielectric nanostructures in order to combine low cost and high efficiency features. Tha last but not less imporant application it can be found within the bio-medical side of nanotechnology. Cancer therapy treatment are both very important applications of science for human health but at the same time very difficult to implement

because of several parameters playing key role. Indeed high cost or good cells destruction are two of the most limiting factor in order to efficiently implement cancer treatment.



FIGURE 2.12: Plasmonic application in the solar cells field from [28]. Here are shown different ways of implementing plasmonic structure for thin film solar cells efficiency improvement: (a) metal nanoparticles on the surface; (b) metal nanoparticles inside the semicondcutor and (c1),(c2) metal nanoparticles or periodic arrays at the interface between metal and semiconductor.

Plasmonic photo thermal theray (PPTT) is based on the light-heat conversion thanks to metallic nanostructured materials among which gold nanoparticles are the most promising candidate. In figure 2.13 (A) it can be seen a schematic picture of tumor tissue treatment on animal. The heat dissipation is a non-invasive way to attack pathogenic agents. Nanoparticles are injected via solution and the area of interest is irradiated by near infrared light causing the localized increasing of temperature. Several nanoparticle shapes can be adopted allowing different wavelength absorption and also different functionalization. The latter is very important in order to obtain a higly specific binding to the tumoral cells avoiding the elimination of healty cells. The mostly general concept of functionalization could allow to create a realtheranostic device allowing targeting, therapeutic, diagnostic and moitoring functions on the same platform. The latter is the basic concept for a personalized approach of future medicine where the role of nanotechnology will be of increasing and fundamental importance.



FIGURE 2.13: Plasmonic photothermal therapy for cancer treatment: (A) tissue cancer treatment on animal via laser stimulation and (B) functionalization of differentrly shaped nanoparticles and the following adhesion to carcinogenic cells. [29]

Chapter 3

Simulation: COMSOL Multiphysics®

In this chapter a simple simulation of the EM field amplification is shown first for a single NP and then for a couple of leaned NPs. Using [30] guide it can be first modelize the nanosphere scattering. From this example it can be modeled the NPs scattering, before and after leaning. Silicon dielectric function is taken by Comsol database from [31] whereas regarding gold and silver [22] paper has been used. The COMSOL electromagnetic simulation is used in order to compute the scattered field from the NPs structure after an incident plane-polarized wave such that the electric field vector is tangential to the NPs surface, that is having only x and y components:

$$\mathbf{E}_0 = E_0(-\sin\phi, \cos\phi, 0) \exp(-i(k_x x + k_y y)) \tag{3.1}$$

This model is based on a 3D electromagnetic, frequency domain (ewfd) solution from the wave optics folder. Differently from [comsol reference], the model presented here provides only the distribution of the electric field from an incident field in a "full field formulation" and is not a combined solution of an incident field seen as a background field and the scattered field seen as a perturbation of to the total field used by a "scattered field formulation" presented in [reference]. In this full field solution two ports (top and bottom) are set up: one defines the incoming wave allowing for specular reflection whereas the other absorbs the transmitted plane wave. The latter is achieved by means of perfectly matched layers (PML) which are insert in the two ports. PML are essentially non-reflecting, absorbing all the outgoing waves from the input and output port. Anyway PML are not considered boundary-condition but only mesh domains with complex permittivity and permeability. The side boundaries relies on Floquet conditions stating that the solution on the two sides of the geometry are equals but for a complex phase factor. In this way an infinite geometry is created.

Comsol computation starting point is

$$\nabla \times (\nabla \times E) - k_0^2 \epsilon_r E = 0 \tag{3.2}$$

The general parametes used for building up the NPs structure and simulate the orthogonal incident field are in table 3.1. In order to get familiare with COMSOL, the first attempted geometry is a simple sphere made of gold. Figure 3.1 shows the EM field distribution of a 30 nm radius sphere excited at 520 nm, since its resonance peak it is known to be around this wavelength from literature [32]. In this case the metal structure is put inside a spherical domain in order to exploit its symmetric structure.

Name	Value	Description
W	350 [nm]	width of physical geometry
h_0	430 [nm]	thickness of physical geometry
t _{pml}	150[nm]	PML thickness
n _a	1	Refractive index, air
wl	$\approx 680 \text{ nm}$	pprox 100 nm
φ	0	Azimuthal angle of incidence
θ	0	Polar angle of incidence
Io	$1 [MW/m^2]$	Intensity of incidence field
Р	$I_0^* w^{2*} \cos(\theta) = 1.225 e^{-7} \mathrm{W}$	Port power
E ₀	$sqrt(I_0*Z0_{const})$	Incident electric field

TABLE 3.1: Comsol general parameters.

After parameters initialization, system geometry has to be defined. Before defining the proper NP geometry it is very importante to create the domain where our NP will be analyzed under the plane wave excitation. Indeed it is very important to create a domain as close as possible to the NP surrounding it. Basically for tow reasons: the first one quite straightforward, that is computation time saving whereas the second one relies on the physical modelization, that is the scattered light outgoing from that nanostructure will vanish in short distance range, so that it will be impossible to detect renonance events if not working really close to the "scatterer".



FIGURE 3.1: COMSOL first example: Au sphere having 30 nm radius at 520 nm laser wavelenght.

Working on a 2D plane the starting point is an ellipse which has to be modified in order to avoid too much sharp region at the connection between the silicon rod and the metal cap. As a matter of fact, spikes and very sharp elements are very sensitive to LSP resonance having a very high amplification factor. This would create artifacts in the EM field amplificaton correspondoning to a non-real structure, since NPs have smooth metal caps. Then the Si rod has to be created inside the metal cap. Afterwards a 360° revolution of the 2D geometry leads to a perfect NP element.

Pillar height h_p	Pillar tip heigth h_t	Pillar diameter d	Semi-axis a	Semi-axis c
635 [nm]	100 [nm]	40 [nm]	62 [nm]	155 [nm]



TABLE 3.2: NP size parameters from [33].

FIGURE 3.2: NPs size parameters from [33].

After that the material selection has to be done. COMSOL has a wide database from which any needed material can be chosen. In this particular case gold and silver characteristics belong to the famous [22] paper regardind optical properties of such metals. Whereas silicon optical properties are chosen from [31] as already said. All the other simulation regions are characterized by air properties. The next step involve mesh creation. Comsol relies on FEM, which basically works by solving the main equations of the modelization in every system small region. Thus system geometry has to be discretize, possibly creating finer mesh structure where fundamental region are present.

The only very important constrain ruling the mesh creation in this particular system is the maximum size of each mesh element which should be $d \le 6/\lambda$. This condition connecting the element size with the incoming wavelength depends on the physical phenomen of resonance described in the previous section. Dimensions and sizes of NPs are taken from [33] describing a structure like the one in figure



FIGURE 3.3: NPs mesh.

3.2. The mesh obtained for a NPs couple is shown in figure 3.3. It can be seen that the two NPs are kept inside a domain really close to them and that the boundaries are made by five layers, allowing the PML condition to absorb the scattered field reducing reflections. The mesh element are finer at the NPs structure whereas are less fine for the external domain.



FIGURE 3.4: Au (A) and Ag (B) single NPs illuminated with a $\approx 1\mu W$ at 780 nm. The highest enhancement is obtained for Ag as it is expected. And silver shows a larger field at the bottom part of the cap (cavity mode) as shown by the reference [33]. Whereas gold has a more uniformly distributed field on its cap surface.

Figure 3.4 shows both gold (A) and silver (B) single NP. As already mentioned from theoretical considerations, from the electric field distribution it can be seen that silver has the lergest amplification. The figure shows electric field distribution respect to the incident field E_0 . Thus both for Au and Ag the field has been enhanced, but silver has a larger enhancement. It can be also seen that for silver electric field is more concentrated at the region where is the junction between silicon rod and the metal cap. This is called the cavity mode and it is due to collective oscillation of electrons inside that bottom part of Ag cap strongly coupling with the Si rod due to small cap diamater (40 nm) compared to the excitation wavelength (780 nm) [33]. Having a look at figure 3.5 it can be still said that silver presents stronger field enhancement. The most imporante information coming out from figure 3.5 is that the LSP resonance it is amplified due to NPs leaning effect. The latter is the simulation proof of NPs' powerful design. From [33] we know that both Au and Ag NPs have two resonance mode and here in figure 3.5 it has reproduced that at 780 wavelength laser excitation the larger field intensity of silver respect to gold it is not only due to the material properties but also to the excitation of the strongest mode that is the cavity mode. As a matter of fact figure 3.5 (B) shows silver having the electric field distributed at the neck between silicon and silver experiencing the cavity mode excitation exploiting the largest field amplification. Therefore the effective strenght of the leaning effect it is also shown by a simulation approach.



FIGURE 3.5: Au (A) and Ag (B) leaned NPs couple illuminated with a $\approx 1\mu W$ at 780 nm. The EM field at the closest point between the two NPs is five times greater than the single NPs maximum EM field, showing the creation of the EM hotspot. The highest enhancement is obtained for Ag like in the single NPs as it is expected. And silver shows a larger field at the bottom part of the cap (cavity mode) as shown by the reference [33].

Chapter 4

Fabrication

This chapter will be focused on the fabrication procedure. The following description will show one of the core points of the whole work inside which is enclosed the attractive power of the anti-counterfeit application of this device: the process simplicity, which leads to a fast and cost effective fabrication. The process relies on two-steps [1, 24]:

- Nanopillars (NPs) fabrication using anisotropic RIE (reactive ion etching);
- Metal-cap creation on top of the NPs by means of metal evaporation (e-beam evaporation for Au and thermal evaporation for Ag);

4.1 **Process overview**

All the fabrication step has been performed inside an ISO 5 standard 14644-1 (class 100) cleanroom location belonging to DTU Danchip, Denmark national micro and nano-frabrication center. The following description will present process parameters already optimized in order to create a NPs substrate having the characteristics described in table 4.2.

Diameter	Туре	Dopant	Resistance	Thickness	Orientation
4"(101,6 <i>mm</i>)	n	Phosphorous	$1-20~\Omega cm$	$525\pm25~\mu m$	<100>

TABLE 4.1: Silicon wafer characteristics



FIGURE 4.1: Silicon wafer

Starting from a silicon wafer described in table 4.1 the first step is a mask-less etching using the ASE (advanced silicon etcher) which will be described more in details in the next paragraph. This will lead to a NPs structure on the whole wafer. After that the NPs tips will be covered with metal by means of evaporation (e-beam evaporation for Au or thermal evaporation for Ag). Therefore the final result is a NPs structured wafer needed to be cut into smaller chips ready to be used for Raman spectroscopy analysis (the usual purpose) or as in this study in order to manipulate molecular spectra in different way to overcome competitive binding and control the shapes of different Raman maps.[34]



FIGURE 4.2: Nanopillars fabrication and metal (Au) coverage.

With the process parameters describe in the following sections the optimized structure obtained and used in the whole thesis work has the characteristics described in table 4.2.

NPs density	NPs height	NPs width
$pprox 19 \mu m^{-2}$	$pprox 680 \ \mathrm{nm}$	pprox 100 nm

TABLE 4.2: NPs average characteristics

The total process time needed for one 4" Si wafer is roughly: 20 min at ASE + 1 hour at the metal evaporator = around 1:30 hour. From a single 4" wafer, eight (1 x 1) cm chips can be extracted from the center of the wafer, avoiding bord effects. The total process is shown in figure 4.3.



FIGURE 4.3: NPs complete fabrication process: (A) the maskless RIE process produces a NPs structure (B) which is covered by a metal (C) so that the final metal-cap NPs structure is obtained (D).

4.2 Silicon plasma etching

In dry etchants, the etch reactants come from a gas or a vapor-phase source and are typically ionized. There two kinds of dry etches: plasma and non-plasma based. In this thesis it has been used the plasma based etching technique. The latter uses the generation of reactive ions or free radical species by electron bombardment at low pressure. The usage of dry etchants leads several advantages: eliminates handling of dangerous acids and solvents and gives the possiblity to have isotropic or anisotropic etch profiles. Whereas using plasma reactions can be performed at lower temperature than termally driven reactions. Plasma is really often called as the fourth state of matter and it is essential in many nanotechnology process, either for surface modification either for nanostructures creation. The latter nanoscale application regards the case of the present master thesis work, where a plasma etching process is used to obtain a nanopillars nanostructure. This fabrication process exploit both the most important plasma features for nanoscale applications: ions creation and acceleration toward the sample surface and the ability to produce chemically active species (radicals) at low temperature.

4.2.1 Theory

Plasma is a very complex substance and its physical description deals with the complex interaction of many charged particles with external or self generated electromagnetic field. The following description will regard low temperature plasmas where the ionization degree $\alpha = \frac{n_e}{n} \approx 10^{-6} \div 10^{-4}$ (n_e : electron number density; n = gas number density) is pretty low. Here we limit our description to the very basic behaviour of plasma in order to represents a specific nanofabrication procedure. Plasma is an excited gas formed by: electrons, ionized and neutral atoms or molecules, ionized and neutral radicals and photons. Free radicals are electrically neutral species that have incomplete bonding and are extremely reactive (e.g. SiO, SiH_3 , F). The creation of this kind of complex mixture can be depicted by means of the Townsend mechanism: starting by the formation of a free electron at the cathode due to an external force, e.g. a magnetic field (as in this case where an ICP has been used), whose path to the anode will generate others electron-ion pairs. This will lead to a cascade effect: the new electrons will be consequently accelerated, creating new electron-ion pairs. The total production of electron-ion pairs depends on electrode separation and the total gas pressure. If the kinetic energy exceeds the threshold for ionisation, new electrons can be produced. Townsend suggested an empirical relation for α / p :

$$\frac{\alpha}{p} = C_1 exp(-C_2 \frac{p}{E}) \tag{4.1}$$

C1 and C2 are constant for a special kind of gas and limited range of reduced electric field strength. On the other hand, the generated positive ions are accelerated in opposite direction towards the cathode. The breakdown voltage in terms of the product pd_E represents the well known Paschen law. The characteristic Paschen minimum of the breakdown voltage represents optimal relation between α/p and E/p. Therefore the Paschen law gives the minimum voltage needed to maintain a discharge between two planar parallel electrodes.



FIGURE 4.4: Townsend condition and Paschen's law

The latter description is valid for a plasma created from a DC gas discharge at low pressure. The machine used in this thesis works by means of an ICP (inductively coupled plasma) discharges exploiting a solenoid in which a RF (13.56 MHz) current is flowing, producing a time variant magnetic field B(t) and an induced, non conservative electric field E(t). Therefore the description is slightly different but it is still based on the concept of a breakdown voltage to be reached in order to create a self sustained plasma discharge depending on the product pd and in this case also on the product ωd . In this case an inductive resonant coupling is exploited in order to accelerate electrons and create the avalanche process to reach gas ionization. electrons keep on colliding with the ambient neutral gas particles and sufficiently high energy (highly accelerated) electrons keep on creating new charges and eventually gas breakdown occurs. At the driving frequency of 13.56 MHz principally only the electrons follow the RF field and gain energy, whereas the heavy ions remain too immobile reacting to such a fast change and remain at room temperature. Due to the collisions, electrons following the (accelerating and decelerating) RF cycles are knocked out (of the field lines) with a resultant increase in thermal energy. In absence of collisions oscillating electrons will have no gain or loss of energy on an average.

With an RF alternating potential the polarity is changing on the bottom electrode. In principle the electrons will be attracted to the bottom electrode when the polarization is positive and the ions will be attracted when the electrode is of negative polarization. But when the frequency of the alternating potential is very high (radiofrequency level) the ions are too heavy to travel across the plasma in that time frame only the electrons will reach the electrode. At equilibrium: most of the time the bottom electrode will be negatively charged and the electrons will be repelled from the bottom electrode and therefor almost no electrons exists in the nearest region of the electrode. This part is called the ion sheath. No collisions with electrons will happen here including the excitations and therefor no light is coming out from this part. It is therefore also called the dark space. Only when the cathode potential is above zero electrons will flow to the bottom electrode. Because of the average potential difference between the plasma and the bottom electrode the ions coming into the Ion sheath are accelerated toward the bottom electrode and will bombard a sample laying on that electrode. The larger a V_dc the stronger the bombardment will be. This ion bombardment is involved in the etching process and gives the physical contribution to the etch [34].

Collisions in the gas:	
lonization: A + e -> A ⁺ + 2e	Dissociation: AB + e -> A + B +e
Excitation:	Recombination:
A + e -> A* + e	A + B -> AB
A* -> A + hv (light)	A+ + B + e -> AB

FIGURE 4.5:	Reactions	inside	plasma
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If we take a closer look at the collisions (table 4.4) that takes place in the plasma we have:

- 1. The Ionization where an atom or molecule will loss and electron and become a positive ion and the extra electron will participate in collision processes.
- The Excitation where an electron will be excited to and outer electron shell in the atom and after a while it will relax again by sending out light – this is what makes the plasma glow.
- 3. But we also have an dissociation when the electron energy is higher than the bond dissociation energy of the molecule. These free atoms are called radicals and they are very reactive. An example of this that is very used in plasma etching is the dissociation of CF_4 .
- 4. Also some recombination will take place.

4.2.2 Etching process: general mechanism

Plasma is the energy source replacing heat and high temperature in this kind of nanofabrication process. Now we will see all the different main steps driving the etch mechanism on silicon.



FIGURE 4.6: Plasma etching mechanism. [35]

- 1. The radicals or the reactive species are created in the plasma by dissociation.
- 2. These radicals are not electrically charged and will therefore move around by diffusion.
- 3. Some will get close enough to the sample surface to be adsorbed on the surface.
- 4. A reaction may take place between the sample and the radical to form a reaction product.
- 5. The reaction product may desorb from the surface.
- 6. And the product may diffuse into the plasma to be pumped out.

Alogens gas are used because of their 2 fundamental properties for this application:

- They can be introduced as gas (either as diatomic gas or in combination with another atom).
- They are reactive and are likely to form volatile reaction products.



S= Sample surface material

FIGURE 4.7: Plasma etching mechanism, ions role. [35]

Here we see the sample surface material which is illustrated with the blue atoms. The red dots are the reactive species. The gray dots are species that do not react or do not form volatile reaction products with the sample. The roles of the ions are:

1. The ions bombard the surface to remove the non reactive species – this leaves room for the reactive species to diffuse onto the surface.

- 2. When the ions bombard the surface they help activating the reactions. Some reaction do not need it but others do.
- 3. The ion bombardment also has the role of helping the reaction products to desorb from the surface.

4.2.3 NPs etching process

Finally we can describe the peculiar process on which the nanopillars structure fabrication is based on. Using plasma etching combined with the passivation technique it is possible to obtain anisotrpic etching using a combination of an isotropic etchant gas (SF_6) plus O_2 which will protect sidewalls from being removed so that the etching process becomes anisotropic and nanopillars structures can be obtained. After that an O_2 cleaning treatment is needed in order to eliminate all RIE byproducts. The already well developed fabrication process was invented by Michael Stenbæk Schmidt, a "Nanoprobes" group member belonging to the Micro and Nanotechonoly depertmant of DTU. This process is based on the black silicon method [black silicon reference] but without using a lithographic step, that is without using a resist protection of the substrate, but only by means of direct exposure of the surface.



FIGURE 4.8: Etching step.

Passivation

So far we have only talked about the gases for etching – but we also mentioned one of the etch mechanisms for anisotropic etching is based on using a passivation gas together with the etch gas. The passivation gas deposits a thin layer all over the substrate or on the material to be etched. Then the role of the ions is to sputter away the layer in the horizontal plane leaving the passivation layer on the sidewalls. The neutrals then get access to etch the substrate only in the horizontal plane thereby producing an anisotropic etch profile. This is used for many materials but it is especially valuable when etching with a gas chemistry that is isotropic in nature. For example silicon etching with fluorine chemistry. As we have talked about, the etching of Si with fluorine will occur without ion bombardment and is only enhanced slightly with the ion energy.

Temperature	$SF_6: O_2$ flow ratio	Platen power	Pressure	NPs formation rate
-10 °C	1.12	120 W	36 mT	3 nm/s

TABLE 4.3: RIE process parameters

Therefore passivation is needed. The passivation can either happen simultaneously with the etching or it can be done in a so called Bosch process where the etch step and passivation steps are alternating fast.

So for etching only with SF_6 , SiF_4 is formed in an isotropic etch. When adding O_2 to the gas a layer of siliconoxyfluoride will form on the silicon. To continue etching an ion bombardment is needed to sputter of the layer and open it up for the fluorine atoms to get access to the Si to form silicon fluoride. The ions only sputter off the horizontal layer of silicon oxyfluoride and not the sidewalls and therefore the etch becomes anisotropic. To prevent contamination in the subsequent SERS spectra, the silicon nanopillars were manufactured without the fluorocarbon passivation cycles normally used in deep reactive ion etching and reported in.

SF ₆ etching	O ₂ cleaning	
04:00 s	00:30 s	

TABLE 4.4: ASE etching recipe

The process is self-masking by means of passivation: using a specific SF_6 : O_2 ratio (table) it can be obtained at the same time an isotropic etching, an anisotropic etching and a passivation from the O_2 . The combined effect of:

- 1. F^- radicals: isotropic silicon etching forming volatile SiF_4 ;
- 2. O^- : silicon passivation forming SiF_xO_y ;
- 3. S^+ ions: anisotropic silicon etching;



FIGURE 4.9: Passivation mechanism.

Gives rise to the black silicon which is the origin of nanopillars. There is a constant competition between the fluorine radicals that etch and the oxygen radicals that passivate the silicon. At a certain oxygen content there is such a balance between the etching and the passivation that a nearly vertical wall results. At the same moment native oxide, dust, etc. will act as micromasks and, because of the directional etching, spikes will appear. These spikes consist of a silicon body with a thin passivating silicon oxyfluoride skin. They will become higher in time and, depending on the etch rate, they will exceed the wavelength of incoming light after some time. This light will be 'caught' in the areas between the spikes and cannot leave the silicon surface any more. So, all the light is collected by the etching surface and it is turned black [36, 37].

O₂ plasma cleaning

After the creation of NPs an oxygen plasma based cleaning step is needen in order to get rid of all etching byproducts, essentially SiF_4 .

Temperature	O_2 flow	Platen power	Chamber pressure
-10 °C	45 sccm	20 W	10 mT

TABLE 4.5: O_2 plasma cleaning treatment

4.2.4 **RIE equipment**

The reactive ion etching (RIE) is performed using the surface technology systems MESC multiplex ICP advanced silicon etcher (ASE) showed in figure 4.10. In the ICP chamber, a coil is wound around the upper part of the chamber which is made of a nonmetallic material (here ceramic) so that the magnetic field easily penetrates into the chamber. If an RF generator is connected to the coil, it generates a cylindrically symmetric magnetic field that changes polarity with the RF generator. If a gas is introduced into the chamber, electrons will be ripped off* the atoms and start to oscillate back and forth while the atoms remain relatively immobile (they are much heavier than the electrons). The process is similar to one in the RIE chamber, but here there are no electrodes inside the chamber. This enables us to obtain high density plasmas without problems of corrosion and power lost through dissipation. The plasma created by the coil does not have any preferred direction (the RIE plasma did have one because of the grounded upper electrode). An RF generator is therefore connected to the platen electrode so that ions from the plasma may be driven towards it in order to assist in the etching process. The magnetic field induces an electrical current in the plasma that flows so as to oppose the RF magnetic field (in the same way as in any transformer etc.). This is why this plasma is referred to as an Inductively coupled plasma. *When a time-varying electric current is passed through the coil, it creates a time-varying magnetic field around it, which in turn induces azimuthal electric field in the rarefied gas, leading to the formation an electron trajectories providing a plasma generation

In figure 4.11 a system overview it can be seen. Here you can see that the process gasses are lead into the chamber through Mass Flow Controllers (MFC) to control the flow rate. The pressure in the chamber is measured with the pressure gauge and controlled by the pressure controller. The pressure controller is a valve in the



FIGURE 4.10: ASE scheme and the actual equipment in Danchip cleanroom at DTU campus.

pumping line that can be more or less open. The platen is cooled by the chiller. Coil power and platen power are connected to the coils around the chamber and to the platen electrode.

More than the ICP system, the main elements of ASE are depicted in figure 4.11. All gas sources are conncted to the main chamber which pressure is controlled by a dedicated gauge. Pump and chiller are fundamental in order to change from atmospheric pressure down to the operation pressure and in order to mantained the desired pressure and temperature of the pressure. In figure 4.12 it can be seen the clamping/cooling systems in the dry etchers. In the TDESC (Thick Dielectric Electro Static Chuck) the wafer is positioned on the ceramic surface. The part in the lower left image is positioned underneath the chuck in the upper image. At the edge 5 pins may lift the wafer to enable transfer of the wafer. The wafer is electrostatically clamped to this chuck during processing. The chuck is cooled or heated by a liquid running inside the chuck. To transfer the heat between the chuck and the wafer He gas is let in underneath the wafers from below. It comes out of the middle hole and goes though the pinholes and spreads to the recess at the edge of the chuck. The He is set to a pressure of 10 Torr. This will keep a He pressure underneath the wafer while He will leak out at the edge. The He leak up rate is measured before the etch starts and if it is too high the wafer is not properly clamped and the process will fail. This ceramic chuck is quite robust and can withstand a O2 plasma but with any particles on the chuck the wafer cannot clamp properly and you will see high He leak up rates.



FIGURE 4.11: ICP chamber scheme of the ASE. [35]

4.3 Metal evaporation

The second and last main step of the fabrication process is the metal deposition on top of the NPs by means of metal evaporation. This step is fundamental in order to exploit the localized plasmonic resonance enhancing effect for SERS.

Deposition rate	Chamber pressure	Optimized thickness for 785 nm laser
10 Å/s	$2 \cdot 10^{-6}$ mbar	(225 ± 5) nm

TABLE 4.6: Metal evaporation parameters

4.3.1 E-beam evaporation

In e-beam evaporation a powerful electron beam is created by applying a high voltage to a filament and sending a strong current through it. Magnets direct the e-beam from the filament onto the material that the user wants to evaporate. The material is placed in a pocket in a circular copper heath. One material can be evaporated at a time. The pocket with the material being evaporated is called the source.

The electron beam heated evaporation source, as used for high technology thin film fabrication (figure 4.13) has 3 basic sections: the electron gun, the beam deflection magnetic lens, and the evaporant plant. The beam is formed in the gun, passes through the magnetic lens and is focused upon the evaporant. Application of an electron beam heated source is governed by three complex rela-

Application of an electron beam heated source is governed by three complex relationships:

1. The energy balance of the evaporant charge and the requirement for stable dissipation of the beam energy;



FIGURE 4.12: Clamp and cooling system of the ASE

- 2. The complex distribution of the evaporant vapour flux from the evaporant surface caused by the pressure within this vapor and the resultant evaporant surface geometry;
- 3. The ionizing effect of the electron beam, as it passes through the evaporant vapour cloud, impacts the melt surface and is partially reflected from the surface;



FIGURE 4.13: E-beam evaporator scheme.[38]

For useful evaporation to occur, the evaporant surface must reach a temperature such that the surface vapour pressure is greater than 10-1 Torr. At very high evaporation rates, this pressure may reach 10 Torr. The electron beam is conventionally

accelerated to 10 kV at a current of up to 1.5 A. This beam impacts an area of 1/4-1 cm2 with an energy of up to 60 kW/cm2. Stable evaporation requires that a thermal equilibrium exist in the evaporant and the energy dissipation must be stable. Energy is dissipated from the evaporant principally by conduction to the hearth, then by evaporant phase change heat and least by thermal radiation. A portion of the beam, often containing considerable energy, is also reflected from the evaporant surface [38].

E-beam evaporation equipment

The evaporation regarding Au (or Al) has been performed using a Temescal FC-2000 e-beam evaporator from Ferrotec shown in figure 4.14.



FIGURE 4.14: Temescal e-beam evaporator.

As in the other equipments the procedure here is the same: venting the first chamber to reach atmospheric pressure and insert the sample. Afterwards having mounted the samples, pumping down. Temescal system takes approximately 30 minutes in order to reach the working pressure of 1e - 6 mbar. Then the right recipe has to be selected corresponding to the right material and then the deposition can start.

4.3.2 Thermal evaporation

Deposition of thin films from resistance heated evaporation sources was the first practical thin film deposition technique. Since then, despite being technologically eclipsed by electron beam heated evaporation sources and sputtering, resistance evaporation finds wide use, offering a unique combination of reliability and economy.

Thermal evaporation equipment

Concerning Ag deposition, the Kurt Lesker thermal evaporator system for metals has been used. Figure 4.16 shows the general scheme of a therma evaporator. In the main chamber there is the substrate holder on the top where each sample can be mounted, even several 4" wafers at the same time, but also smaller chips. Then

there is the shutter opening during the deposition procedure. The source is mounted below in a in contact with the heating element, which is a metal resistance. The latter being the core of the entire system. In general they are made by refractory metal (Mo, Ta, W) in three design classes: coils, boat and special ones. Their desings are of crucial importance in order to fulfill three fundamentals requirement: evaporant compatibility, capacity and power availability. The most difficult to achieve is the compatibility since several important evaporants (Au, Fe, Al) dissolve all refractory metals in a certain way.



FIGURE 4.15: Thermal evaporator.

The Lesker equipment used during this work is shown in figure 4.15. The screen on the left controls the pressure gauges and systems, while the screen on the right controls processes and receipes from power point of view guiding the rise power and the soak power.



FIGURE 4.16: Thermal evaporator chamber scheme from [38].

Chapter 5

Characterization techniques

In this thesis work two main characterization techniques are used: SEM to analyze the structural quality of the SERS device and Raman spectroscopy in order to get information about the molecules deposited on top of the surface both from gaseous and liquid phase.

5.1 SEM: scanning electron microscopy

The NPs structure characterization is based on scanning electron microscopy. The aim of this characterization is to verify the NPs quality and dimensions in order to be mathced as much as possible with the fabrication settings. The most important features to be checked with SEM are:

- NPs dimension: this parameter has to be matched with fabrication adn simulation prediction in order to LSP resonance to be exploit in connection with the Raman equipment laser excitation wavelength;
- Metal-cap quality and homogeneity;

Moreover it will be shown in the images section the device leaning mechanism comparing the before and after ethanol solution exposure. The following section will present a brief review of electron microscopy theory and the equipment description.

5.1.1 Theory

Electron microscopy is one of the most widely used characterization technique in the nanotechnology field. Shrinking the dimension of devices and structures, the optical wavelengths diffraction limit has been overcome switching from visible lights (optical microscopy) to electrons, having smaller wavelength with respect to visible photons, thus allowing the resolution of micro and nano world objects. The diffraction limit affecting optical microscopy means simply that in order to resolve an object the incident wavelength has to be less than the object size itself. Therefore optical lights ranging from around 400 nm to 800 nm cannot be used in order to see object. Considering $E = \frac{p^2}{2m_e} = \frac{h^2}{\lambda^2 2m_e}$ the De Broglie relation allows us to express the electron wavelength and compare it with the optical one.

$$\lambda = \frac{h}{p} = \frac{h}{m_e v} \tag{5.1}$$

For electrons we get $\lambda \approx 0.4$.

Thus the comparison in terms of resolution can be done using the Rayleigh criterion expressed in the equation 5.1 where d is the aperture diameter and $\alpha << 1$ is the aperture angle.[39]

$$d \approx 0.61 \frac{\lambda}{\alpha} \tag{5.2}$$

Finally we have a difference of about four order of magnitude regarding resolution: ≈ 300 nm for optical and ≈ 0.4 nm for electronic.

The interaction between the impinging primary electron beam with the sample surface gives rise to several different type electrons coming out from the sample, each one bringing a different information contribution from a different sample region. The interaction volume, as can be seen from figure 5.1, has a peculiar shape made by several electron types and also from the characteristic x-rays. The main electrons types are:

- primary electrons: incident electron beam coming from the microscope electron source having a fixed, tunable energy;
- in-lense SE(1);
- in-chamebr SE(2);
- backscattered electrons;

We will focus on secondary electrons SE for the NPs characterization, especially on the SE1, being the one with the best resolution, because coming from the sample surface. They are generated by interactions between incoming electrons and sample surface atoms. They are emitted from a surface area corresponding to the spot size of the incoming electron beam. Whereas the SE2 are generated by backscattered electrons that have returned to the surface after several scattering events, emitted from a surface are larger than the incoming spot size, that is coming from a deeper sample are.



FIGURE 5.1: On the left the impinging primary electrons beam and the consequent different types of electron coming from the sample surface. On the right the electrons interaction volume. [40]
5.1.2 Equipment

All the measurements were taken using a SEM Supra 40 VP (2010) from Zeiss. The latter has four different electron types detectors: in-chamber SE, in-lense secondary electrons, four quadrant backscattered electrons (QBSD) and variable pressure SE (VPSE). Ranging from 20 V up to 30 kV concerning accelerating voltage and with a theoretical resolution of 1 nm(@ 15 kV) and 1.9 nm (@ 1 kV) for high vacuum mode and 2 nm (@ 30 kV) for variable pressure mode.



FIGURE 5.2: SEM supra from Zeiss.



FIGURE 5.3: SEM supra column scheme [40]

5.1.3 Images

The following images have been taken using setting the parameters shown in table 5.1 and giving rise to NPs structure characteristics in according to table 4.2 of the previous section. These images show NPs structure according to the table 4.4 recipe and are covered by 225 nm of Au.

Electrons	Vacuum mode	Accelerating voltage	Working distance
In-lense	High vacuum	8-15 kV	4-5.5 mm

TABLE 5.1: SEM measurements characteristics.

Figure 5.4 shows the result after the first fabrication step: the black silicon substrate which will be covered by metal to form the NPs. There is not a precise ordere structure because the pillars growht is quite randomized, but the pillars height is equal among them.



FIGURE 5.4: SEM black silicon side view.

In figure 5.5 the final result can seen: the nanopillars substrate has been fabricated, ready to be used. The rounded shape metal caps now is covering the pillars creating an ellipsoidal-like geometry on top of the pillar. The metal layer is also covering the bottom part of the substrate creating a metal support for each of the NPs. The average height it is easily computer by means of Zeiss SEM software tools. In figure 5.6 it can be easily seen the not-uniform distribution of NPs ensemble thanks to the view from above. After leaning there will be clusterized regions of NPs where analytes can be easily trapped contributing to signal enhancement.



FIGURE 5.5: SEM Au-cap NPs side view.



FIGURE 5.6: SEM Au-cap NPs top view.

5.2 Raman spectroscopy

Raman spectroscopy is the main analytical technique used in this thesis and it has already been introduced in chapter 2. Here we focus only on the Raman microscope apparatus used in the whole work. The main results from Raman measurements will show in the next section "Results and discussion".

5.2.1 Equipment

All the Raman measurements have been done using the DXRxi Raman microscope from Thermo Fischer instruments by setting the parameters showed in table 5.2.

Objective	Power	Scanning t	λ	Aperture	Pixel size
10 x	2 mW	0.05 s	780 nm	50 µm	100 µm



TABLE 5.2: Raman measurements parameters.

FIGURE 5.7: DXRxi equipment from Thermo Fischer.

Figure 5.8 shows the Raman microscope scheme. A laser source is directed to the sample surface in order to excitate it and collected by an optical microscope. The notch filter is needed to eliminate the laser component from the scattered light, because we are interested into anelastic scattering, giving signal at wavelengths different from the laser. The scattered light is then focused through the microscope until it reache the diffraction gratings, which is needed to separate each different spectral components to be finally analized by the CCD camera.



FIGURE 5.8: Micro Raman apparatus scheme.[41]

The way Raman spectrum are analized is based on the concept of "Raman shift". During the next chapter all the spectrum plots will have this Raman shift in on the x-axis expressed in terms of $[cm^{-1}]$ as is typically done in the spectroscopy fashion. This parameter is related to the difference between the incident and the scattered wavelength during the anelastic event as follows:

$$\Delta\omega(cm^{-1}) = \left(\frac{1}{\lambda_0(nm)} - \frac{1}{\lambda_{vib}(nm)}\right) \cdot \frac{(10^7 nm)}{cm}$$
(5.3)

Where λ_0 is the incident laser wavelength whereas the λ_{vib} is the wavelength belonging to the vibrational state where the scattering has take place. Therefore in this way using the expression of photon energy E = hv where the frequency is $\frac{c}{\lambda}[s^{-1}]$ and the wavevector $k = \frac{1}{\lambda}[cm^{-1}]$ the wavevector difference can be related to the energy difference using v = ck and finally with:

$$\Delta E = h\Delta\nu = hc\Delta k \to \Delta k = \frac{\Delta E}{hc}$$
(5.4)

Chapter 6

Results and discussion

This is the core section of the entire work. Here will be shown all results coming from different approaches of molecules deposition on top of the SERS NPs device. The first attempt is based on molecules deposition by evaporation followed by a metal layer coverage. In this way three molecules have been deposited showing good spectrum cleareance. The second approach is easier and less time consuming than the first one, giving better results in term of spectrum and maps. This methods is based on ethanol molecules mixture direct deposition on NPs surface using micropipette leading to ≈ 0.5 cm diameter circular drops staying on top of the chip surface. The last approach is based on the idea of reducing the deposited droplets size using a nanoplotter, that is a droplets dispenser working in the range of nano/pico liters. This tool gives ≈ 0.5 mm drops diamater. Therefore more droplets can be deposited on the same 1 x 1 cm chip leading to the possibility of encoding some patterns e.g. letters are shown. During the first section of this chapter is focused on the characteristics which the molecules needed for our purpose should have. The following sections will devoted to analyze features and experimental results for each one of the three different approaches.



FIGURE 6.1: Representation of molecules embedding concept.

6.1 Molecules

Molecules we are dealing with need to have several features in order to be used matching with our NPs structure:

- Good Raman cross section: Raman active group has to be present (e.g. benzene ring and similar);
- Good bonding with gold or silver;
- At least one spectrum peak not overlapping each others;
- Volatile (only for metal layers approach);

Since the Raman effect relies on scattering a fundamental properties for a moelecule to give a good Raman signal in terms of intensity is to have an high Raman scattering cross section. The latter parameter describes the scattering activity of an analyte. One general definition for the scattering cross section can be done starting by the simpl differential cross section expression:

$$\sigma' = \frac{d\sigma}{d\Omega} = \frac{I_S}{I_0} \tag{6.1}$$

Which is the ratio between the scattered light intensity and the incident light intensity. Therefore the total scattering cross section can defined as following (like we already defined in section 3):

$$\sigma_{S_{tot}} = \int_0^{4\pi} \left(\frac{d\sigma}{d\Omega}\right) d\Omega \tag{6.2}$$

The differential Raman cross section which we are interested in is related to square of the transition polarizability tensor and to the fourth power incident light and vibrational mode wavenumber difference:

$$\sigma' \propto (\tilde{\nu}_o \mp \tilde{\nu}_{vib})^4 (\alpha)_{fi}^2 \tag{6.3}$$



FIGURE 6.2: Thiol based molecules. [42]

Where $\tilde{\nu}_o$ is the wavenumber of the incoming radiation and $\tilde{\nu}_{vib}$ the one of vibrational mode, in spectrography notation in which $\tilde{\nu} = \frac{1}{\lambda} = \frac{f[Hz]}{c}$ are valid. The latter dependencies of the scattering differential corss section comes out from a very long and complex quantum mechanical dissertation. [43, 44, 45]

The most important thing is to understand the why a molecule can be more or less desirable for a Raman or SERS application. Therefore we can asses that molecules with an easily polarizable electron cloud have an high scattering cross section. The molecules used in this work are shown in figure 6.3 because they shows good Raman signal intensity given that molecules with aromatic or conjugated functional group have the delocalized electrons which are easily polarizable. [44]

This σ_{scatt} analysis concerning molecule behavior is needed in order to quantify the Raman signal intensity coming among different molecules. Whereas the σ_{scatt} done in chapter 3, concerning the NPs structure has been done with always in order to achieve a bettere understanding of the quality an object has in terms of scattere, but in with different purpose. As a matter of fact in chapter 3 the scatter ability of NPs was studied for better understanding their LSPR behavior in order to amplify the signal coming from any anylite, as a contribution exploiting the SERS effect.



FIGURE 6.3: Molecules: (A) thiophenol; (B) 2-Furanmethanethiol; (C) trans-1-(2-pyridyl)-2-(4-pyridyl)-ethylene (also know as BPE).

The latter disccusion accomplish the aim to be working with the choice of molecules regarding Raman signal intensity. But what about the affinity between molecules and the substrate ? In figure 6.2 on of the most used molecules class for SERS application is shown: the thiols. These molecules are very common because of the covalent nature of the S-Au bond which helps trapping molecules on the substrate surface either in gaseous and liquid phase leading to device good performance in terms of SERS signal.[46] The second reason why this kind of molecules are widely used is still strictly connected to Au. Especially for bio-sensing is Au has a good biocompatibility and also a strong resistance to oxidation. [47, 48] In the following analysis, one peak for each molecule has been chosen as a reference, by Raman spectroscopy. These peaks allows to clearly identify a molecules amont the others two, beacause none of these is overlapping with others. Table 6.1 shows all three characteristic peaks.

Thiophenol	2-Furanmethanethiol	BPE	
$418 \ cm^{-1}$	$1493 \ cm^{-1}$	$1200 \ cm^{-1}$	

TABLE 6.1: Molecules characteristics SERS peak chosen in this work.

6.2 Metal multilayers approach

The first approach is based on the idea of overcoming competitive binding among the thiol-based molecules and other probe molecules as BPE. As we already said in the previous section, the covalent nature of the S-Au binding make thiols surface adhesion very strong and put this molecules on a preferencial role. As we will see, without any specific attention, thiophenol and furanthiol would kick out BPE from the SERS substrate. Therefore with successive metal layer deposition, (... disegno del NPs con diversi starti e 3 molecole). As a matter of fact while thiol group can exploit the binding strenght of covalent bond, BPE linking with the Au NPs cap relies on the lone pair electrons of pyridyl nitrogens. [48] Another important feature to exploit this method is to use evaporation for the first molecules while use liquid deposition only at the end. Because since the enchancement effect is linked with the leaning of NPs due to tension forces while the solutio is evaporating, we want exploit the enchancement only at the end of our process. Therefore we need volatile molecules to be deposited. In table 6.1 the vapor pressure values from the chemicals database kemibrug.com are shown.

Thiophenol	2-Furanmethanethiol		
1.93 mmHg	2.89 mmHg		

TABLE 6.2: Molecules vapour pressure values.

6.2.1 Procedure

First of all a NPs structure 4" wafer is fabricated, depositing 180/200 nm of metal. In this way starting from 180/200 nm the optimized thickness of 225 nm can be reache depending if it is the case of 2 molecules or three molecules deposition. Therefore starting from a 4" NPs wafer, using a diamond tip pen, 4 chips of 1x1 cm are made from the wafer center, avoiding edge effects. The NPs structure formed on the edge of the chip is affected by defects. Then the first method follows the procedure described in figure 6.4. The first molecule, which it always has been thiophenol during the experiments, is evaporated putting in suspention a 1x1 cm chip by means of an "elephant foot" experimental tool like the one in figure ... under a fumehood.



FIGURE 6.4: Suspension tool.

After this, a first layer of metal (Au or Ag) is deposited. As already said, depending on the 2 or 3 molecules case, the first layer thickness is of 25 nm or 20 nm, in order to reach 200 nm or 225 nm as intermediate step for the 3 molecules case or as the final step for the 2 molecules case. Then if it is the case of 2 molecules, a drop of BPE solution is deposited on the chip surface and the Raman measure can be performed. Otherwise a second evaporation is done using the second molecule, that is 2-furanmethanethiol. After that a second metal layer 25 nm thick is deposited on the surface and finally the BPE drop can be spot on the device. Also in this case the NPs SERS substrate is ready to be analyzed under the Raman apparatus.



FIGURE 6.5: Metal multilayer procedure scheme: evaporation of first molecule; metal layer deposition; second molecule evaporation; third molecule solution deposition.

In the following sections about results, Raman sepctra and mpas will compared taking as a reference for each molecule the characteristic peaks shown in table 6.1.

6.2.2 Results for 2 molecules

In this section the result from a first experiment section is discussed. This first experiment's result is shown in figure 6.6. Starting from the bottom of plot (A) the BPE spectrum is shown with its characteristic peak at $1200 \ cm^{-1}$ highlighted. Going up the second spectrum (green) belongs to thiophenol. The $418 cm^{-1}$ peak also is highlighted. As it can be seen, none of the two chosen characteristic peak overlaps with another different peak of the other molecule. Finally the blue spectrum on top of figure 6.6 is the composite spectrum where each one of the two peak can be clearly distinguished among the other. Looking at the map, it can be seen that most of the BPE signal sits in the inner circle, while the thiophenol signal is distributed over the whole drop surface. As we will see later, this couldn't have be possible without the metal interlayer, because the BPE signale would have be almost absent or very low, because of competitive binding.



FIGURE 6.6: Thiophenol evapoporated (5min) + 25 nm Au + BPE 100 μ M. (B) Raman maps. From left to right: thiophenol; BPE.

6.2.3 Results for 3 molecules

In this second the second important result has been achieved, another molecule has been added. Thus using this metal multilayer strategy, 2 molecules can be successively evaporated on top of the NPs platform, with alternating metal layer. Whereas the third molecule is added by a $1\mu L$ droplet deposition. Analyzing figure 6.7 starting from the lwoer part of the plot, in the same way we already did from figure 6.6 it can be seen spectra of each single molecule: 2-furanmethanethiol (yellow); BPE (orange) and thiophenol (red). Afterwards the green spectrum is the intermediate step, that is the spectrum of both thiophenol and 2-furanmethanethiol. In this spectrum either the 1483 cm^{-1} and the 418 cm^{-1} peaks are clearly visible and not overlapping. The last (blue) spectrum is the final spectrum after a $1\mu L$ droplet of 10 mM BPE solution deposition.





(B)

FIGURE 6.7: Thiophenol evaporated (5min) + 25nm Au + (15 min) furanthiol evaporation + 20 nm Au layer + BPE 100 μ M. (B) Raman maps. From left to right: thiophenol; 2-furanmethanethiol; BPE.

6.2.4 Ag vs Au competitive binding

The whole previous analysis has been done only for Au, because Ag showed a different behavior making impossible the metal multilayer approach. Differently from Au, using silver after the thiophenol evaporation, the first metal coverage and the BPE droplet deposition, the BPE was almost absent.

- Motivi per cui quindi non c'è la parte di metal multilayer dedicata al Ag.



FIGURE 6.8: Thiophenol evaporated on Au NPs chip and then a 1 μ L drop of 10mM BPE solution. (A) Thiophenol evaporated (1 min); (B) Thiophenol 418 cm⁻¹ after BPE drop; (C) BPE 1200 cm⁻¹.

By comparing figure 6.8 with figure 6.9 it is easily to understand why Ag NPs structure it has not shown during the metal layer approach study. Even by inserting a metal layer after the evaporation of thiophenol, as we usually have done in the metal layer approach, the BPE signal is only slightly increased.



FIGURE 6.9: Thiophenol evaporated on Ag NPs chip and then a 1 μ L drop of 10mM BPE solution. (A) Thiophenol evaporated (1 min); (B) Thiophenol 418 cm^{-1} after BPE drop; (C) BPE 1200 cm^{-1} .



FIGURE 6.10: Thiophenol evaporated on Ag NPs chip and then a 1 μ L drop of 10mM BPE solution having a 20 nm Ag layer in the middle. (A) Thiophenol 418 cm^{-1} after BPE drop (1 min evaporation); (B) BPE 1200 cm^{-1} .

6.3 Molecules mixed solution approach

In this section, based on different solution preparation, it is explained also how the BPE solution used in the previous section is prepared. This method shows a faster and cheaper procedure respect to the previous one, because any other fabrication step is required. Moreover tuning the relative concentration inside each solution the spectra peaks relation and the Raman maps shape can be tuned very easily. Therefore using this method a unique label creation can be achieved by the simple deposition of one $1\mu L$ solution droplet.

6.3.1 Procedure

In this work all solution are based on ethanol as solvent. Starting either from solid, either from a liquid phase molecule, an ethanol solution can be prepared. The very simple and fundamental relation guiding us in making a solution is the following one:

```
Mass[g] = Concentration[mol/L] \cdot Volume[L] \cdot Formula \ weight[g/mol] (6.4)
```

Thanks to the letter equation starting from a solid phase chemical (BPE it comes out as a yellow crystal powder) a 10 mL solution in vial of a desired concentration can be done, only calculating the required mass from (6.4).

Value	Thiophenol	Furanthiol	BPE
Formula weight [g/mol]	110.18	114.17	182.22
Density [g/mL]	1.073	1.132	

TABLE 6.3: Molecules formula weights and density.

Instead, if one starts from a liquid phase molecule and that's the case for thiophenol and 2-furanmethanethiol, the simple relation $V = \frac{m}{\rho}$ where ρ is the molecule density, has to be used. In this case from (6.4), imposing a volume and a concentration of e.g. 10 mL and 10 mM, the required chemical mass it can be computed. Afterwards using the density value from table 6.3 the required volume of liquid from one molecule is obtained.



FIGURE 6.11: Sartorius Quintix micro balance used for BPE weigh.

6.3.2 Au molecules mixture

The firs interesting result coming out this second approach is not only that we are able to obtained the same result (even better in terms of spectrum clearness) as the metal multilayer scheme, but the fact that we can tune both the spectrum and the map by adjusting the relative molecules presence inside the solution. In figure 6.12 we can see starting from the bottom a 33/33/33 percentage mix solution of both 10 mM BPE/thiophenol/furanthiol. This solution shows a predominant signal coming from thiophenol, a small signal coming from the furanthiol presence whereas a nearly absence (at least in the inner circle part of the droplet spot) of BPE. That's because of competitive binding. This will be analyzed later more in detail. Decreasing thiophenol "strength" by decreasing its presence inside the solution we can observe in the second spectrum (green) that now BPE is clearly visible, whereas the whole thiophenol spectrum have been decreaed. Even furanthiol gain a stronger presence in the total composite spectrum. The final spectrum corresponds to a 75/20/5 balancing of the three molecules. This proportion has been chosen as the most balanced, because each characteristic peak lies almost at the same signal intensity. This solution has been chosen as the sample/proof solution for further comparisons and dissertations. Therefore this method can be surely be favorable respect to the metal layers in terms of time and cost (metal evaporation is not cheap). Moreover two key concepts are achieved thanks to the "proportion tuning":

- competitive binding overcoming without metal layers embedding;
- map shapes control as degree of freedom for anti-counterfeit purposes;



FIGURE 6.12: Au samples. Comparison among different proportion $1\mu L$ drop 10 mM mix solution. Starting from the bottom (BPE/furan/thiophenol): 33/33/33; 70/20/10; 75/20/5.

Starting from the bottom furanthiol, BPE and thiophenol spectra are shown. The corresponding maps are the first three at the bottom row (furanthiol, BPE and thiophenol from right to left). The center group represents two molecules mixture. Starting from the lowest dark green: BPE/thiophenol; thiophenol/furanthiol; BPE/furanthiol. The same order is valid in order to read the Raman maps: starting from the bottom the second, third and fourth row represent the (left/right) BPE/thiophenol; thiophenol/furanthiol; BPE/furanthiol maps. The last three spectra group on top of the plot regards, in order starting from the bottom: metal multilayer three molecules composition, molecules mixture in 75/20/5 proportion and the normalized sum starting from the single molecule spectrum done using Matlab (will be explained better in a deedicated section forward). Finally the last maps starting from above: the first three regards the 75/20/5 mix solution (as in figure 6.8 on top) and the second three regards, the three molecules metal multilayer (same as figure 6.7).

In the multilayers approach the whole spectrum has the weakest signal and even each peak is not perfectly clear as in the other two mixed spectra. Comparing the mixed spectrum and the normalized sum it can be seen that the result is almost equal. The spectrum is clear and each peak is perfectly visible.



FIGURE 6.13: Au samples. Comparison among: single molecule solutions, two molecules mixture solutions, three molecules mixture solutions, three molecules with metal layers method and the single molecules normalized sum. Every solution is $1\mu L$ drop 10 mM mix solution and the multilayer method parameters (exposure time and metal thickness) are the same of figure 6.6.

6.3.3 Ag molecules mixture

As in the case of glod NPs substrate, also for silver samples the same behavior is shown. Increasing the concentration of BPE with respect to furanthiol and thiophenol the 1200 cm^{-1} peak is increased and at the same time the signal intensitiy coming from the map is increased for BPE. The same "proportion tuning" concept is applicable for AgNPs. But differently from Au, furanthiol helps the BPE to sit inside the droplet already from the 33/33/33 proportion solution. Then increasing the BPE presence in the solution, also the intensity signal map changes giving a more ditributed signal inside the drop extension.



FIGURE 6.14: Ag samples. Comparison among different proportion $1\mu L$ drop 10 mM mix solution. Starting from the bottom (BPE/furan/thiophenol): 33/33/33; 70/20/10; 75/20/5.

Figure 6.15 shows the same comparison we have already done for Au, except for the metal multilayer case, as stated before.

This silver case shows the same concepts shown for gold, except for the BPE/thiophenol behavior which will be explained deepr in the next section. Figure 6.15 shows indeed the possibility to use silver in order to create a very peculiar and complex label, using a single drop of solution. Silver is more convenient for the cost and for its signal intensity, which is greater than the one achievable in gold. But silver has the drawback of being easily oxidazible. Therefore peculiar chip protection methods have to be devoleped.



FIGURE 6.15: Ag samples. Comparison among: single molecule solutions, two molecules mixture solutions, three molecules mixture solutions and the single molecules normalized sum. Every solution is $1\mu L$ drop 10 mM mix solution.

6.4 Au vs Ag

In this section the main differences between gold and silver samples spectrum are under analysis. First of all the signal intensity. Figure 6.16 shows AuNPs (top) and AgNPs spectra from the three molecules mixture. The signal coming from the AuNPs being magnified by a factor of 8 in order to be compared with the Ag spectrum. Therefore the signal coming from Ag is higher, as we already said. This is because the LSPR peak is much closer to the laser exciting wavelength of 780 nm for silver than from gold. As a matter of fact AgNPs resonance peak lies around 800 nm whereas for AuNPs it stays around 850 nm.

The latter statements come from scattering section measurements already done during the NPs optimization and characterization done in the Nanoprobes group. [24] The second important difference has already been treated in 6.2.4 so here we can go further stating that not only for the evaporation plus metal layer method, silver has a different behavior regarding competitive binding, but also in the case of mixed solution. Raman maps in figure 6.17 show Au (top) and Ag (bottom) spectra for BPE/thiophenol mix solution. We can easily see that for Ag, BPE is literally pushed out from the presence of thiophenol (maps on the rigth column belong to BPE, left shows thiophenol map), thus BPE is confined in the outern region of the deposited droplet. That's not the case of gold, where BPE lies also in the inner circular region.



FIGURE 6.16: Au (top) and Ag (bottom) three molecules mix solution comparison.



FIGURE 6.17: Au (top) and Ag (bottom) BPE/thiophenol mix solution comparison.

6.5 Nano plotter approach

The last approach used in this study is based on the usage of the GeSiM nanoplotter 2.1 (figure 6.18). Usually this equipment is used for bio application such as array based diagnostics and immunoassays. []

In our case the using this tool we aim to reduce the dimension of the drops we are able to dispense on NPs device surface and precisely control their distribution on it. Showing this possibility will be the key point in order to understand the possibility for creating controllable micro pattern made by different molecular species on top of NPs. In this way a new possibility of encoding information by means of this SERS platform will open, leading to letters, number and codes in general (e.g. bar codes, QR codes) to be written in order to achieve a very high encription level.



FIGURE 6.18: GeSiM nanoplotter 2.1.

Table 6.4 shows the nanoplotter parameters used in order to achieve the Raman map in figure 6.19. This figure is made using a gold substrate by depositing 38 drops of a 10 mM BPE solution. The available tips for this tool have a volume range from 0.35 to 0.06 nL. Our results are based on the nanoliter tip, which is the largest in volume. Using this tip we were able to achieve a spot pitch (distance between two spots) of 1 mm. This allowed the deposition of a larger number of drops on a single 1x1 cm NPs chip. Thus 38 drops are at the same time in a 1 x 0.4 cm area.

Tip type	Drop volume	Tip-sample distance	Pitch	Deposition time
Nanoliter tip	$\approx 0.4 \text{ np/drop}$	4 mm	1 mm	1 min

TABLE 6.4: Nanoplotter parameters.

The minimum achieavable pitch depends on the nature hydrophobicity of the surface: hydrophobic sample allows a 0.3 mm maximum pitch whereas hydrophobic substrate allows a 0.1 mm maximum pitch. The NPs platform is hydrophobic towards ethanol ([33]) that is drops tend to spread on the surface. Therefore this is not the best type of surface in order to achieve the less possible drop pitch. The latter issue plus the drop dependence on the cubic radius ($V = \frac{4}{3}\pi r^3$) let not possible to judge the exact volume from the spot diameter seen on the chip. And also because the diameters in flight are not necessarily the same as the final spot diameters on the surface. That's why the drop volume is given approximately in table 6.4.

Th spacing between spots is constant and also the spot shape and size are. Therefore figure 6.19 assure the possibility to achieve our purpose in order to create a proper pattern. Further studies are needed in order to reduce each spot size using the pico liter tip and also to minimize the spot pitch. Looking at the spectrum shown in figure 6.19 it can stated that even the spectrum quality for each spot is good. Indeed comparing this spectrum with the first appearing BPE spectrum on a gold sample (figure 6.6) we can see that they are exactly the same. This means that even the same characteristic peaks tuning shown during the previous ection of this chapter could in principle be done using more than one molecule.



FIGURE 6.19: "IDUN" written with a 10 mM BPE solution using the nanoliter J tip. On the right the BPE average spectrum belonging to the spots.

6.6 Spectra and normalization

During this entire chapter we analyzed many spectra from many samples, but where they come from ? Using the DXRxi Raman microscope software called OMNICxi it is possible to obtain the average spectrum from a selected area. These average spectrum were the objects of our study, coming from the drop area deposited on the NPs chip substrate.

A second clarification for the data treatment has to be done concerning the spectra normalization using Matlab. Starting from the single molecule spectra (BPE, thiophenol and 2-furanmethanethiol) and by summing up them together, it can be obtained a prediction of the final 3-molecules composite spectrum (figure 6.13 and 6.15). As a matter of fact by comparing the normalized sum with respect to the 3-molecules composite spectrum there is a good correspondance. This comparison it is possible by a simple normalization obtained using the following procedure. The normalized 3-molecules composite spectrum obtained from the sum of the original experimental single molecules spectra in the case of the 75/20/5 BPE/furanthiol/thiophenol mix solution is:

$$MIX_{75,20,5} = \alpha(thiophenol) + \beta(2 - furanmethanethiol) + \gamma(BPE)$$
(6.5)

Each weighting factor has been computed as:

 $\alpha = \frac{\text{thiophenol } 418 \text{ } \text{cm}^{-1} \text{ peak in the } 3 - \text{molecules experimental solution spectrum}}{\text{thiophenol } 418 \text{ } \text{cm}^{-1} \text{ peak in the single molecule experimental thiophenol solution spectrum}}$ (6.6)

 $\beta = \frac{furanthiol\ 1500\ cm^{-1}\ peak\ in\ the\ 3-molecules\ experimental\ solution\ spectrum}{furanthiol\ 1500\ cm^{-1}\ peak\ in\ the\ single\ molecule\ experimental\ furanthiol\ solution\ spectrum}}$ (6.7)

 $\gamma = \frac{BPE\ 1200\ cm^{-1}\ peak\ in\ the\ 3-molecules\ experimental\ solution\ spectrum}{BPE\ 1200\ cm^{-1}\ peak\ in\ the\ single\ molecule\ experimental\ BPE\ solution\ spectrum}}$ (6.8)

Whereas concerning the 2-molecules spectra we used:

$$MIX_{75,20} = \frac{\beta + \gamma}{2} (furanthial / BPE experimental mix solution spectrum)$$
(6.9)

$$MIX_{75,5} = \frac{\alpha + \gamma}{2} (thiophenol/BPE experimental mix solution spectrum)$$
(6.10)

 $MIX_{20,5} = \frac{\alpha + \beta}{2} (thiophenol/fur anthiol experimental mix solution spectrum)$ (6.11)

Chapter 7

Conclusions and outlook

7.1 Summary

Chapter 1 presents the aim of this work, giving information about the need of higher security level labels and an overview on presente state-of-the-art SERS anti-counterfeiting labels. Afterwards the working principle of the NPs substrate developed by "Nanoprobes" group at the micro and nano-technology department at DTU is explained and then some SERS applications of it are shown. Chapter 2 is focused on the theoretical background cocnerning Raman spectroscopy and its combination with plasmonic leading to the SERS effect. Chapter 3 shows how it is possible to simulate NPs substrate behavior using COMSOL multiphysics. Chapter 4 explain the fabrication process with all the steps and parameters involved into it, starting from a brief theory introduction to an overview of the cleanroom equipment. Chapter 5 is focused on the SEM and Raman microscopy characterization from a technical point of view. Chapter 6 is the key section of this work, showing the procedure and the different strategies used during this six months period at DTU leading to the development of an attractive and potentially commercial SERS based anti-counterfeiting label platform. Solutions preparation, molecules deposition, measurements and results are expleined in this section. Starting from a metal multilayer approach, going to a solution direct deposition and finally getting to a demonstration of a possible pattern (letters) deposition which can act as "codes" all the interesting and promising results have been presented. The first strategy allows to use evaporation as a deposition method. The strongest bonding molecules (Au/Ag - S covalent bonds) can be deposited by evaporation whereas weaker bonding molecules can be deposited in much higher concentration usind deposition in solution. In this way competitive binding can be overcome. The second strategy allows for a much more easier and fast molecules deposition having where the spectrum changes can be done tuning molecular proportion in the solution. In this way not only the spectrum relative intensity peak can be tuned, but also the Raman maps can be changed allowing a unique characterization of the deposited solution spot. Final experiments further improve the direct deposition method using a nano dispense equipment allowing the possibility of controllable, reliable and precise direct deposition of molecular solutions making possible pattern creation only visible at the Raman microscope. Thus giving the chance to create unique and complex labels using both spectral complexity and encoding feature.

Finally this section presents a summary of the developed work together with an overview on future development of this platform which would lead to a reliable and affordable real world application, Compatible with high volume manufacturing.

7.2 Outlook

The results obtained in this thesis show the potential of creating a unique and stateof-the-art platform for anti-counterfeiting purposes. But this is still the first step in order to achieve the cost-effectiveness to achieve mass production. In order to do so few fundamentals steps are required:

- material improvement: replacing Al instead of Au and Ag, will allow to create mass production attractive devices at a very low cost fabrication. Its availability would lead to very cheap wafer fabrication;
- packaging: packaging has to be studied in order to protect the fragile silicon substrate and really thin metal layer, thus giving as final result really reliable and durable labels. This packaging should satisfy at the same time physical protection and optical access for incident and scattered light requirement. In this way the label would be unchanged and accessible for external reading and check;
- pattern size and resolution: reduce the possible pattern dimension that can be deposited. Concerning the nanoplotter: shrinking the spot dimension and pitch by means of the pico-liter tip would allow higher resolution (compared to the one of present advanced but expensive SERS labels from [9, 8, 3]) and smaller features thus allowing larger encoding capacity;
- multiple molecules solution for complex patterns deposition;

From [49] we can see that despite the advantage on cost, aluminum has high ϵ_2 values in the optical range that is has high losses figure 7.1 (B). Figure 7.1 shows the comparison among real and imaginary part of aluminum dielectric function with Au and Ag $\epsilon(\lambda)$ from [49].

Moreover combining both controllable pattern deposition and molecular mixtures would give the possibility of creating really complex and hard to force labels using spectral mixing and codes writing.



FIGURE 7.1: Real (A) and imaginary (B) part of Au (gold), Ag (silver) and aluminum (Al) dielectric function with respect to wavelength from [49].

In the last part of the previous section we have seen some hints suggesting that very easy and cheap method cna be used to reduce the drop size increasing the resolution. Thus the next step will be creating complex and small patterns combining different molecules solution at the same time. In this way a very powerful platform can be obtained. Concerning the package issue in [50] it has been presented an example of how this can be done. In this paper the combination between electroplating and lithography has shown to be leading to an effective coverage for a SERS system as can be easily observed in figure 7.2 b). As a matter of fact it can be seen that NPs has been covered in a contact-less way. The latter procedure is well estabilished in the orifice plate fabrication for integrated print head in inkjet printers. This method is shown to be low cost and replacing conventional multi-level packaging approach. Another promising option could be using the epoxy based material shown in [51] which seems to involve an easier ppackaging procedure, but the application on NPs surface has to be studied to verify the contact effect between the epoxy layer and the nanostructured nanopillars, problem that in the previous case doesn't have to be faced with. The latter is aimed to be applied into photonic devices packaging, showing good light transmittance into the visible range were plasmonic materials are working.



FIGURE 7.2: NPs SERS device packaging example.[50]

Finally it can be said that using this SERS base labels in combination with new generation Raman portable devices (figure 7.3 shows an example of the actual portable spectroscope) could lead to a large spreading of this platform. Given its high security level and the actual implementation of noble metals, the application of this labels could even be thought for luxury and precious good market like jewels and paintings only.



FIGURE 7.3: Example of portable Raman spectroscope from Bruker.

Bibliography

- Michael Stenbæk Schmidt, Jörg Hübner, and Anja Boisen. "Large area fabrication of leaning silicon nanopillars for Surface Enhanced Raman Spectroscopy". In: *Advanced Materials* 24.10 (2012), pp. 11–18. ISSN: 09359648. DOI: 10.1002/ adma.201103496.
- [2] European Union Intellectual Property Office. URL: https://euipo.europa.eu/ ohimportal/it.
- [3] Yejing Liu et al. "Flexible Three-Dimensional Anticounterfeiting Plasmonic Security Labels: Utilizing Z-Axis-Dependent SERS Readouts to Encode Multilayered Molecular Information". In: ACS Photonics 4.10 (2017), pp. 2529–2536. ISSN: 23304022. DOI: 10.1021/acsphotonics.7b00796.
- [4] Vincenzo Giannini et al. "Plasmonic Nanoantennas: Fundamentals and Their Use in Controlling the Radiative Properties of Nanoemitters". In: *Chem. Rev.* 111.6 (2011), pp. 3888–3912. ISSN: 0009-2665. DOI: 10.1021/cr1002672. URL: http://dx.doi.org/10.1021/cr1002672.
- [5] Sebastian Schlücker. "Surface-enhanced raman spectroscopy: Concepts and chemical applications". In: Angewandte Chemie - International Edition 53.19 (2014), pp. 4756–4795. ISSN: 15213773. DOI: 10.1002/anie.201205748.
- [6] Leicester Le et al. "PhD Thesis". In: IEEE Communications Surveys and Tutorials 44.4 (2015), pp. 2046-2069. ISSN: 1539-9087. DOI: 10.1109/SURV.2013. 031413.00127. arXiv: arXiv:1011.1669v3. URL: https://www.sophos.com/ en-us/medialibrary/PDFs/technicalpapers/sophos-current-state-ofransomware.pdf{\%}OAhttps://www.verisign.com/assets/report-ddostrends-Q42015.pdf{\%}OAhttp://ieeexplore.ieee.org/lpdocs/epic03/ wrapper.htm?arnumber=7430287.
- [7] Eric Le Etchegoin Pablo Ru. *Principles of Surface Enhanced Raman Spectrosocopy*. Elsevier, 2009, p. 663.
- [8] Yan Cui et al. "Multiplex plasmonic anti-counterfeiting security labels based on surface-enhanced Raman scattering". In: *Chemical Communications* 51.25 (2015), pp. 5363–5366. ISSN: 1364548X. DOI: 10.1039/c4cc08596e.
- [9] Y Liu et al. "multiplex molecular information for anti-". In: (2016), pp. 4312– 4319. DOI: 10.1039/C6TC00682E.
- [10] Jon Ashley et al. "Quantitative Detection of Trace Level Cloxacillin in Food Samples Using Magnetic Molecularly Imprinted Polymer Extraction and Surface-Enhanced Raman Spectroscopy Nanopillars". In: (2017), pp. 11484–11490. DOI: 10.1021/acs.analchem.7b02725.
- [11] Nanopillars Using Large-area Raman et al. "Surface-Enhanced Raman Bioassay on Aptamer-Functionalized Mapping". In: 6 (2013), pp. 5350–5359.

- [12] Aron Hakonen et al. "Detection of nerve gases using surface-enhanced Raman scattering substrates with high droplet adhesion". In: *Nanoscale* 8.3 (2016), pp. 1305–1308. ISSN: 20403372. DOI: 10.1039/c5nr06524k. URL: http://dx.doi.org/10.1039/c5nr06524k.
- [13] François Lo Presti et al. "The first clinical isolate of Legionella parisiensis, from a liver transplant patient with pneumonia". In: *Journal of Clinical Microbiol*ogy 35.7 (1997), pp. 1706–1709. ISSN: 00951137. DOI: 10.1038/srep45264. URL: http://dx.doi.org/10.1038/srep45264.
- [14] Lidia Morelli et al. "Surface Enhanced Raman Scattering for Quantification of p-Coumaric Acid Produced by Escherichia coli". In: *Analytical Chemistry* 89.7 (2017), pp. 3981–3987. ISSN: 15206882. DOI: 10.1021/acs.analchem.6b04428.
- [15] Nanopillars Using Large-area Raman et al. "Surface-Enhanced Raman Bioassay on Aptamer-Functionalized Mapping". In: 6 (2013), pp. 5350–5359.
- [16] J.-F. Li and J.-C. Dong. "Shell-Isolated Nanoparticles-Enhanced Raman Spectroscopy". In: *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering* (2017). DOI: 10.1016/b978-0-12-409547-2.13288-3.
- [17] Katrin Kneipp et al. "Single Molecule Detection Using Surface-Enhanced Raman Scattering (SERS)". In: *Physical Review Letters* 78.9 (1997), 1667–1670. DOI: 10.1103/physrevlett.78.1667.
- [18] Nanophoton. What is Raman spectroscopy? 2016. URL: https://www.nanophoton. net/raman/raman-spectroscopy.html.
- Stefan Alexander. Maier. Plasmonics : fundamentals and applications. 2007. ISBN: 9781441941138. DOI: 10.1007/0-387-37825-1.
- [20] John D Jackson, A Barbieri Elettrodinamica Classica (Collana Di Fisica Testi E Manuali)(Zanichelli).pdf.
- [21] Heinz Raether. "Raether_2 Plasmon book". In: (). ISSN: 0003-6935. DOI: 10. 1007/BFb0048317.
- [22] P. B. Johnson and R. W. Christy. "Optical Constants of the Noble Metals". In: *Physical Review B* 6.12 (1972), 4370–4379. DOI: 10.1103/physrevb.6.4370.
- [23] Tim Dalgleish et al. [Principles of nano-optics]. Vol. 136. 1. 2007, pp. 23–42. ISBN: 9780521832243.
- [24] Kaiyu Wu et al. "Plasmon resonances of Ag capped Si nanopillars fabricated using mask-less lithography". In: Optics Express 23.10 (2015), p. 12965. ISSN: 1094-4087. DOI: 10.1364/OE.23.012965. URL: https://www.osapublishing. org/abstract.cfm?URI=oe-23-10-12965.
- [25] Katrin Kneipp. "Surface-enhanced raman scattering". In: *Physics Today* 60.11 (2007), pp. 40–46. ISSN: 00319228. DOI: 10.1063/1.2812122. arXiv: arXiv: 1011.1669v3.
- [26] Martin Moskovits and Uni Uersi. "Surface-enhanced". In: July (1985).
- [27] Sergey I. Bozhevolnyi et al. "Channel plasmon subwavelength waveguide components including interferometers and ring resonators". In: *Nature* 440.7083 (2006), pp. 508–511. ISSN: 00280836. DOI: 10.1038/nature04594.
- [28] F. Enrichi, A. Quandt, and G. C. Righini. "Plasmonic enhanced solar cells: Summary of possible strategies and recent results". In: *Renewable and Sustain-able Energy Reviews* 82.December (2018), pp. 2433–2439. ISSN: 18790690. DOI: 10.1016/j.rser.2017.08.094. URL: http://dx.doi.org/10.1016/j.rser. 2017.08.094.

- [29] Alireza Gharatape et al. Engineered gold nanoparticles for photothermal cancer therapy and bacteria killing. Vol. 6. 112. Royal Society of Chemistry, 2016, pp. 111482– 111516. ISBN: 4133363132. DOI: 10.1039/c6ra18760a.
- [30] COMSOL. "Scatterer on Substrate". In: (), pp. 1–28.
- [31] A. A. "Dielectric functions and optical parameters of Si, Ge, GaP, GaAs, GaSb, InP, InAs, and InSb from 1.5 to 6.0 eV". In: SAO/NASA ADS: ADS Home Page (1983). URL: http://adsabs.harvard.edu/abs/1983PhRvB..27..985A.
- [32] Prashant K Jain et al. "Calculated Absorption and Scattering Properties of Gold Nanoparticles of Different Size , Shape , and Composition : Applications in Biological Imaging and Biomedicine". In: (2006), pp. 7238–7248. DOI: 10.1021/jp0571700.
- [33] Kaiyu Wu et al. "Wafer-scale leaning silver nanopillars for molecular detection at ultra-low concentrations". In: *Journal of Physical Chemistry C* 119.4 (2015), pp. 2053–2062. ISSN: 19327455. DOI: 10.1021/jp510073y.
- [34] R. Beig et al. *Lecture Notes in Plasma Physics: Confinement, Transport and Collective Effects.* 2005. ISBN: 9783540252740.
- [35] DTU Danchip. *Dry etching lecture notes*.
- [36] H Jansen et al. "The black silicon method: a universal method for determining the parameter setting of a fluorine- ..." In: J. Micromech. Microeng 5 (1995), pp. 115-120. URL: http://www.iop.org/EJ/article/0960-1317/5/2/015/ jm950215.pdf{\%}5Cnpapers://7b6bd94c-a483-4e3f-bd34-485f8e2f2e27/ Paper/p19.
- [37] Riccardo D'Agostino and Daniel L. Flamm. "Plasma etching of Si and SiO2 in SF6-O2 mixtures". In: *Journal of Applied Physics* 52.1 (1981), pp. 162–167. ISSN: 0021-8979. DOI: 10.1063/1.328468. URL: http://aip.scitation.org/doi/ 10.1063/1.328468.
- [38] D.A. Glocker and S.I Shah. Handbook of Thin Film Process Technology, Volume 2. 1995. ISBN: 9781315893693. URL: http://books.google.nl/books/about/ HandbookofThinFilmProcessTechnology.html?id=JaAuSQAACAAJ{\&}pgis= 1.
- [39] Physical principles of electron microscopy. Vol. 8. 12. 2005, p. 60. ISBN: 978-0-387-25800-3. DOI: 10.3934/dcds.2018221. arXiv: arXiv:1011.1669v3. URL: http: //linkinghub.elsevier.com/retrieve/pii/S1369702105712323.
- [40] DTU Danchip. *Electron microscopy lecture notes*.
- [41] prof. Giorgis. *Electron microscopy lecture notes from "Materials and characterizations for MEMS"*. aa. 2016/2017.
- [42] Fang Sun et al. "Multi-functional, thiophenol-based surface chemistry for surfaceenhanced Raman spectroscopy". In: *Chemical Communications* 53.33 (2017), pp. 4550– 4561. ISSN: 1364548X. DOI: 10.1039/c7cc01577a. URL: http://dx.doi.org/ 10.1039/c7cc01577a.
- [43] R. Baxter et al. "Raman spectroscopy". In: vol. 39. 5. 2008, pp. 561–563.
- [44] Matti Hotokka. "Raman spectroscopy". In: (2002), pp. 1–34.
- [45] Derek a. Long. The Raman Effect: A Unified Treatment of the Theory of Raman Scattering by Molecules. Vol. 8. 7. 2002, p. 611. ISBN: 0471490288. DOI: 10.1002/ 0470845767. URL: http://doi.wiley.com/10.1002/0470845767.

- [46] Lai Sheng Wang. "Covalent gold". In: *Physical Chemistry Chemical Physics* 12.31 (2010), pp. 8694–8705. ISSN: 14639076. DOI: 10.1039/c003886e.
- [47] Evangelina Pensa et al. "The chemistry of the sulfur-gold interface: In search of a unified model". In: Accounts of Chemical Research 45.8 (2012), pp. 1183–1192. ISSN: 00014842. DOI: 10.1021/ar200260p.
- [48] Ansoon Kim et al. "Study of molecular trapping inside gold nanofinger arrays on surface-enhanced raman substrates". In: *Journal of the American Chemical Society* 133.21 (2011), pp. 8234–8239. ISSN: 00027863. DOI: 10.1021/ja200247x.
- [49] Davy Gerard and Stephen K. Gray. "Aluminium plasmonics". In: Journal of Physics D: Applied Physics 48.18 (2015). ISSN: 13616463. DOI: 10.1088/0022-3727/48/18/184001.
- [50] Ning Ge et al. "3D Monolithic Metal Orifice Plate for SERS Application: A Showcase of Low Cost MEMS Packaging". In: Proceedings - Electronic Components and Technology Conference (2017), pp. 937–942. ISSN: 05695503. DOI: 10. 1109/ECTC.2017.93.
- [51] Yan Zhou Yan Zhou and F.G. Shi. "Epoxy-based optically transparent nanocomposites for photonic packaging". In: 9th International Symposium on Advanced Packaging Materials: Processes, Properties and Interfaces (IEEE Cat. No.04TH8742). 2004 Proceedings. (2004), pp. 100–102. DOI: 10.1109/ISAPM.2004.1287997.