Fabrication, simulation and characterization of tunable plasmonic nano antennas

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Fabrication, Simulation and Characterization of Tunable Plasmonic Nano Antennas.

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Abstract

Recently, the interaction of light with metallic nanostructures has become an area of intensive research due to advances in modern fabrication techniques. Unique effects have been observed in plasmonic nanostructures and have found their application in various areas like in the manipulation of light at the nanometer scale, in cloaking, in higher harmonic generation, in optical photolithography, in chirality control of light, as lasers, in biosensing, and in surface enhanced Raman spectroscopy (SERS). Only a few of these research applications have been implemented in commercial devices so far. One of the main reasons for this is that plasmonic resonance frequencies are extremely sensitive to fabrication inaccuracies. Fabrication at the nanometer scale is always subject to defects, such as surface roughness, corner smoothing, implementation of impurities which have a direct impact on plasmon resonance frequencies. Simulations usually use perfectly flat surfaces with homogeneous materials thus associated with ideal properties such as conductivity or refractive index. This creates a discrepancy between the design of optical antennas using simulations and the ones achieved in laboratory fabrication.

Optical antennas are formed by a pair of nanoparticles brought in close proximity. Antennas separated by small gaps create a high electric field enhancement in their gap region. This property can be exploited for biosensing or SERS to improve the detection limit and measure the presence of single molecules. For this it is necessary to create antennas with sufficiently small gaps, to be able to compensate for the defects created during the fabrication process and reach antenna characteristics that are close to the ones predicted by simulations.

In this thesis, we performed simulations with the commercial finite element method software COMSOL MULTIPHYSICS and its radio frequency (RF) module in order to study the near-field and scattering properties of optical antennas with various geometries and to investigate the dependency of the optical response on the antenna geometry parameters. The simulations were used to design and validate the optical characteristics of the antennas produced in the
In order to reach a high field enhancement we fabricated dipole antennas with gap sizes in the sub-5 nm range with a novel fabrication technique. This technique consists in creating gold nanorods by electron beam lithography and opening a gap in the middle by helium focused ion beam milling. The smallest gap we were able to achieve was 3.5 nm. Gap sizes of 5 nm could be reached in a very reproducible manner. The scattered spectra of the antennas were in good agreement with our simulations. The used fabrication technique created redpositions of substrate material which induced a shift of the resonance wavelength towards the infrared for antennas with gap sizes below 7 nm.

In order to be able to tune the optical response of plasmonic antennas after their fabrication, we developed a process to fabricate bowtie antennas on a flexible, chemically stable and transparent substrate (polydimethylsiloxane – PDMS). The gap size of the antenna can be adjusted by applying a strain on the substrate, which will vary the resonance wavelength of the antenna. We demonstrated a resonance shift of -0.81 nm per strain percent applied to the substrate. The fabrication technique was further optimized by achieving antennas on PMMA pillars. In this case we achieved a resonance shift of about -3 nm per strain percent.

The Raman enhancement capability of the fabricated dipole antennas was tested for the detection of brilliant cresyl blue molecules. For technical reasons only a homogeneous molecule coating of the substrate could be achieved. A Raman enhancement of up to 4.5 for an antenna with a gap size of 9 nm was obtained. Simulations showed that the Raman enhancement factor was sensitive to the illumination beam radius as well as the focusing of the beam in the center of the antenna. A Raman enhancement factor between 6 and 12 was simulated for a beam radius between 700 nm and 500 nm, respectively. The measured value of 4.5 can be achieved with simulations having a distance of 200 nm – 300 nm between the center of the antenna and the beam center. A Raman enhancement factor of about $10^3$ has been estimated by simulations for the presence of molecules only on the antenna. This value can be further increased with smaller gap sizes and a matching illumination source.

We believe that the combination of simulations to achieve a good design of antennas with the capability to reach small gap sizes and the possibility to tune the resonance frequency of the antennas by mechanical stretching of the substrate can lead to very promising devices for sensitive biosensing applications.
Résumé

Récemment, l'interaction entre la lumière et les nano-structures métalliques est devenue un domaine de recherche majeur dû à l’avancée technologique des méthodes de fabrication. Des effets uniques ont été observés dans des nano-structures plasmoniques et plusieurs applications ont pu être réalisées dans des domaines aussi divers que la manipulation de la lumière à l’échelle du nanomètre, le cloaking, la génération d’harmoniques d’ordre supérieur, la photolithographie optique, le contrôle de la chiralité de la lumière, les lasers, la détection de bio-molécules, ou encore la diffusion Raman exaltée par effet de surface (SERS). Jusqu’à présent, peu de ces applications ont pu être implémentées dans des produits industriels, car la fréquence de résonance plasmonique est très sensible aux imperfections. En effet, la fabrication à l’échelle du nanomètre implique la présence d’impuretés, de rugosité de surface, d’arrondissement des angles ; des défauts inéluctables qui ont un impact direct sur la fréquence de résonance plasmonique.

Pour des raisons techniques, les simulations effectuées utilisent des propriétés idéales, notamment en terme d’homogénéité des matériaux, de conductivité, d’index de réfraction ou encore de rugosité de surface. Or, ceci conduit à une divergence significative entre le modèle utilisé dans le cadre des simulations et les antennes plasmoniques fabriquées en laboratoire.

Les antennes plasmoniques sont formées par une paire de nano-particules proches l’une de l’autre. Cette proximité produisant une grande exaltation du champ électrique entre celles-ci, on peut exploiter cette propriété afin d’identifier jusqu’à une seule molécule présente dans l’interstice de l’antenne. À ces fins, il est nécessaire de produire des antennes avec des interstices suffisamment petits, d’être capable de compenser les défauts introduits lors du processus de fabrication et d’atteindre des caractéristiques proches de celles obtenues par simulation.

Dans cette thèse, nous avons effectué des simulations avec le logiciel COMSOL MULTIPHYSICS utilisant la méthode d’éléments finis (FEM) et son module « radio fréquence » (RF) afin d’étu-
Résumé

dier le champ proche et la diffusion des antennes plasmoniques ayant différentes géométries et d’examiner la dépendance de leur réponse optique en fonction de leurs paramètres géométriques. Les simulations ont été utilisées pour la conception et la validation des propriétés optiques d’antennes plasmoniques produites en laboratoire.

Afin d’atteindre une grande exaltation du champ électrique, nous avons réalisé, grâce à une nouvelle technique de fabrication, des antennes dipôles dont l’interstice est inférieur à 5 nm. Cette technique consiste en l’élaboration de nano-bâtonnets d’or par lithographie à faisceau d’électrons et l’ouverture de l’interstice en son milieu par usinage avec une sonde ionique focalisée d’hélium (He-FIB). La fabrication d’un interstice de 5 nm s’est avérée aisément reproduicible avec un minimum de 3.5 nm. Le spectre de diffusion des antennes concorde avec nos simulations. La technique de fabrication employée a créé des redépositions de matériaux provenant du substrat qui ont induit un décalage de la longueur d’onde de résonance vers l’infrarouge pour les antennes ayant un interstice inférieur à 7 nm.

Dans le but de pouvoir ajuster la réponse optique des antennes plasmoniques après leur fabrication, nous avons développé un processus de fabrication d’antennes biconiques (bowtie) sur un substrat flexible, chimiquement stable et transparent (polydiméthylsiloxane – PDMS). La taille de l’interstice peut être ajustée en appliquant une contrainte sur le substrat pour faire varier la longueur d’onde de résonance de l’antenne. Nous avons démontré un décalage de la résonance de -0.81 nm par pourcentage d’élongation appliquée au substrat. La technique de fabrication a été optimisée par la déposition de ces antennes sur des piliers de polyméthacrylate de méthyle (PMMA). Avec cette configuration nous avons obtenu un décalage de -3 nm par pourcentage d’élongation.

Le potentiel d’exaltation de diffusion Raman des antennes dipôles fabriquées a été testé dans la détection de molécules de bleu de crésyl brillant. Pour des raisons techniques, seule une couverture homogène du substrat avec ces molécules a pu être testée. Une exaltation de Raman jusqu’à un facteur de 4.5 pour une antenne dipôle avec un interstice de 9 nm a été atteinte. Les simulations ont démontré que ce facteur est sensible à la nature du faisceau lumineux ainsi qu’à la focalisation de ce dernier avec le centre de l’antenne. Un facteur d’exaltation Raman de 6 à 12 a été simulé pour un rayon du faisceau entre, respectivement, 700 et 500 nm. La valeur mesurée de 4.5 peut être simulée avec une distance de 200-300 nm du centre de l’antenne à celui du faisceau. Un facteur d’environ 10³ a été estimé par nos simulations pour la présence de molécules uniquement sur l’antenne. Ce facteur peut être augmenté avec des écarts plus petits et une source d’illumination en phase avec la résonance de l’antenne.
Nous pensons que la combinaison d’un bon design d’antenne plasmonique à l’aide de simulations avec la possibilité d’ajuster la fréquence de résonance par un étirement mécanique du substrat peut produire un dispositif très prometteur pour les applications dans le domaine de la détection de molécules.
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Chapter 1

Introduction

Antennas working in the microwave and radio frequency domain have already proven their great utility in telecommunication. Figure 1.1 shows the basic principle of communication between two dipole antennas. One antenna plays the role of an emitter (green antenna) and converts electric signals into free-space propagating electromagnetic waves which can be converted back into electric signals by an analogous antenna (red antenna). The wavelength of the transmitted electromagnetic signals depends mainly on the dimensions of the green antenna. When the size of the antenna is scaled down to the nanometer range, the antenna is able to work in the visible part of the electromagnetic spectrum. For this reason they are often referred as “optical antennas” [NvH11].

![Network schematic of two dipole antennas. Antennas can act as an emitter (green) or as a receiver (red). The green one on the left is fed by an electric signal which is converted by the antenna to a free-space propagating electromagnetic waves. These waves are then converted back to an electric signal by the red antenna.](image)

Optical antennas have been extensively studied in the last decade due to their unique ability to overcome diffraction limits and manipulate light at the nanometer scale [EB12, Ozb06]. This property makes them attractive for various applications such as cloaking [BLM09], opti-
cal photolithography in the sub-diffraction limit [SSC+06], chirality control of light [VBSV13, CKL+06], higher harmonic generation [KJK+08], color filtering [XWL+10], and laser [CKC+06] to cite only a few of them.

Localized plasmon resonance in the antenna can enhance the electromagnetic field at or near the antenna compared to the strength of the incident field. This is very attractive for plasmonic molecular bio-sensors that consist of metallic nanoparticles spaced by several nanometers [AHL+08, MEM+05, San09, CLS+11] as well as for tip enhanced Raman scattering (TERS) and surface enhanced Raman scattering (SERS) [NE97, ZCY+C07, ZFS+09, TSSH08]. Higher field enhancement is reached for antennas with a small gap size and gives a higher sensitivity for refractive index change of the environment [FM08]. Plasmonic nanosensors have already demonstrated their capability in label-free detection down to a single molecules [AHL+08, HKT+07, ZZY+C06, BBN11]. Those sensors can be used for the trapping and the real time sensing of molecules [SHV08, ZHS+10].

A difficulty is that in practice it is very demanding to fabricate nanostructures with a gap size in the sub-10 nm range. Several methods have already been considered to produce antenna structures: gallium focused ion beam milling [MEM+05, HCG+10], electron-beam lithography [BYL+08], deposition of colloidal particles onto pre-patterned surfaces [SSF+07] for example. In general the control of the gap size of the antenna remains a challenge.

Another difficulty is that the fabrication methods are not able to fabricate flat surfaces at the nanometer scale. Surface roughness and the implementation of uncontrollable defects in the structures lead to a drastic change of the optical properties of the antenna such as its resonance frequency. This creates a discrepancy between the design and the achieved optical properties of the antenna.

The tunability of the gap size of a plasmonic antenna after fabrication can be used to adjust its resonance frequency. This can be exploited to compensate for the effects of the implementation of defects during the fabrication process and the geometrical mismatch due to fabrication inaccuracies. It has already been demonstrated that colloidal particles deposited on a flexible substrate can be used to optically map the strain of the substrate [San09]. However a reliable fabrication technique of optical antennas with a tunable gap size has not been reported yet.

The main goal of this thesis was the fabrication, simulation and characterization of optical antennas with different geometries. We explored three main topics:

1. Exploit different fabrication technologies in order to reliably fabricate antennas with
the smallest possible gaps and demonstrate their ability in biosensing applications.

2. To fabricate optical antennas with a tunable gap, which can be exploited by resonance wavelength tuning with structure post fabrication.

3. Simulate the near field and scattering intensity of optical antennas having various shapes and dimensions and evaluate its accuracy.

This thesis is divided in four main parts. First a description of the theoretical concepts in plasmonics and an overview of the simulation framework is described in Chapter 2. Second, an overview and a comparison of various fabrication techniques and methods used for characterization are presented in Chapter 3. A fabrication study using the helium focused ion beam milling technique and its ability to produce antennas with small gap sizes will be discussed in detail in Chapter 4. In Chapter 5 we will discuss the fabrication of optical antennas on a flexible substrate and the optimization of the tunability of their resonance frequency by mechanical stretching of the substrate. Finally in Chapter 6 we will study the capability of the fabricated antennas for Raman enhanced spectroscopy of molecules.
Chapter 2

Theoretical background and simulations

In the framework of this thesis optical antennas at the nano scale were fabricated and investigated. In this chapter we introduce the interaction and behavior of such tiny metal objects with electromagnetic radiation. First, theoretical derivations of the metall–dielectric interface (section 2.1) and small particles with simple geometries are investigated (section 2.2). Second, because the complexity of the interaction increases with the geometry, simulations have been performed which are used in order to improve the design and better understanding of the optical response of the fabricated antennas.

2.1 Surface Plasmon Polariton (SPP)

Electrons in the conduction band of metals can move freely through the lattice. Those free electrons form a sea of high density ($n \approx 10^{23} \text{ cm}^{-3}$), also called plasma, which can be excited by electromagnetic waves. The quasi-particle responsible of this plasma oscillation is called a plasmon.

Before going into the details of small metallic particles and antennas, the simple bulk metal–dielectric case will be reviewed.

When an electromagnetic field is incident on a metal–dielectric interface, collective oscillation of plasmons, create surface waves which propagate parallel to the interface (see Figure 2.1). Those waves are called surface plasmon polariton (SPP) and can be easily understood by solving the electromagnetic field equations.

The electric field of a propagating electromagnetic wave along a metal–dielectric interface
can be expressed as:

\[ \mathbf{E} = E_0 \cdot e^{i(k_x x + k_z z - \omega t)} \]  

(2.1)

where \( k_{x,z} \) are the \( x \) and \( z \) component of the wave vector, \( \omega \) is the angular frequency of the incident wave and \( t \) is the time. The coordinates \( x \) and \( z \) are depicted in Figure 2.1.

By solving Maxwell’s equations for the electromagnetic wave at the interface between two materials, with relative dielectric functions \( \epsilon_1 \) and \( \epsilon_2 \), with the appropriate continuity relation, the boundary conditions are:

\[ \frac{k_{z,1}}{\epsilon_1} + \frac{k_{z,2}}{\epsilon_2} = 0 \]  

(2.2)

and

\[ k_x^2 + k_{z,1/2}^2 = \epsilon_{1/2} \left( \frac{\omega}{c} \right)^2 \]  

(2.3)

where \( c \) is the speed of light in vacuum. \( k_x \) is the same for both media at the interface (Stockes law). Equations 2.2 and 2.3 can now be solved for \( k_x \)

\[ k_x = \frac{\omega}{c} \sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}} \]  

(2.4)

For the case of a vacuum–metal interface, the loss-free Drude model of electrical conduction can be used to approximate the dielectric constants. i.e.: \( \epsilon_1 = 1 - \frac{\omega_p^2}{\omega^2} \) and \( \epsilon_2 = 1 \), where \( \omega_p \) is
the plasma frequency of the metal [Mai07]. Thus Equation 2.4 can be expressed as follows:

\[ k_{\text{SPP}}(\omega) := k_x(\omega) = \frac{\omega}{c} \sqrt{\frac{\omega^2 - \omega_p^2}{2\omega^2 - \omega_p^2}} \]  

(2.5)

This dispersion relation is shown in Figure 2.2, where the upper curve (green) satisfies Equation 2.4 which correspond to the Brewster angle [PSCE07]. The lower curve (blue) corresponds to the surface plasmon polariton which is tangential to the light propagating in vacuum and is asymptotic to the non-retarded surface plasmon frequency \( \omega_p / \sqrt{2} \). We see that a wave is not able to directly excite a surface plasmon as the light dispersion (solid red curve) does not intersect with the SPP dispersion (blue curve). Light in a medium with higher refractive index, such as glass (dashed red curve), will have its dispersion curved slope reduced. In this case one condition exists where the light dispersion will intersect the SPP dispersion (red circle). This can be fulfilled with light traveling in a prism before reaching the metal–air interface [Ott68].

![Figure 2.2: Dispersion relation of a surface plasmon propagating along an interface separating a lossy metal described by the Drude model from a vacuum.](image-url)
2.2 Localized Surface Plasmon (LSP)

A Localized Surface Plasmon (LSP) is the result of the confinement of a Surface Plasmon in a nanoparticle of a size comparable to or smaller than the wavelength of light used to excite the plasmon. In the presence of an external electric field, the nanoparticle will polarize itself which will create a dipole

\[ \mathbf{p} = \alpha \mathbf{E}_0 \]  

(2.6)

where \( \alpha \) is the particle polarizability and \( \mathbf{E}_0 \) the incoming electric field. Generally the polarizability is frequency dependent and a function of the dielectric constant of the metal and of the surrounding medium, as well as of the particle geometry. Electric fields near the particle's surface are greatly enhanced. This enhancement falls off quickly with distance from the surface. The particle's optical extinction has a maximum at the plasmon resonance frequency. For noble metal nanoparticles this occurs at visible wavelengths [MCFV06].

In 1908 Gustav Mie solved the extinction and scattering cross section of spherical particles in function of their radius [Mie08]. With this result and the assumption that the bulk wavelength dependent dielectric function of the metal can be applied to a small metal sphere, he was able to explain the beautiful colors of stained glass.

2.2.1 Small metallic particles

For very small metallic particles compared to the wavelength, the electric field can be considered homogeneous over the whole particle.

Mie developed a theory for spherical particles which was generalized by Richard Gans in 1912 to ellipsoidal particles in the quasistatic regime. For an ellipsoidal metallic particle of dimension \((a, b, c)\) (see Figure 2.3), the polarizability \( \alpha \) is given by [BH07]:

![Ellipsoidal shape](image)

**Figure 2.3:** Ellipsoidal shape having half axis dimensions of \((a, b, c)\).
2.2. LOCALIZED SURFACE PLASMON (LSP)

\[
\alpha_i = \frac{4}{3} \pi \varepsilon_0 abc \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_m + L_i (\varepsilon_1 - \varepsilon_m)}, \forall i \in \{1, 2, 3\} \tag{2.7}
\]

where \(\varepsilon_m\) corresponds to the dielectric function of the environment and \(\varepsilon_1\) to the one of the metallic particle. \(L_i\) is a geometry factor equal to \(\frac{1}{3}\) for a perfect sphere and \(L_1 < \frac{1}{3}\) for particles elongated along the \(x\)-axis. The polarization is maximized when

\[
\varepsilon_1 = \varepsilon_m \left( 1 - \frac{1}{L_i} \right) \tag{2.8}
\]

The absorption \(C_{\text{abs}}\) and scattering \(C_{\text{sca}}\) cross sections can be determined as shown in Equation 2.9 [BH07].

\[
C_{\text{abs}} = \frac{2\pi}{\lambda} \text{Im} \{\alpha\} \quad \text{and} \quad C_{\text{sca}} = \frac{8\pi^3}{3\lambda^4} |\alpha|^2 \tag{2.9}
\]

An example of the Mie scattering from a gold ellipsoid having a size of \(130 \times 35 \times 20\) nm\(^3\) in vacuum is shown in Figure 2.4. The resonance is at 710 nm.

**Figure 2.4:** Absorption and scattering cross section of an ellipsoid, having a size of \(130 \times 35 \times 20\) nm\(^3\), in air is calculated using the Mie-Gans theory. Note that both curves use a different scale and that the absorption cross section is largely dominant over the scattering cross section.
Plasmons form standing waves inside the metallic ellipsoids at resonance. The resonance wavelength is then expected to be proportional to the arm length of the ellipsoid. Calculation of the resonance wavelength of gold rods having both short axes equal to 40 nm and a different long axis length is show in Figure 2.5. The results can be fitted with a line having a slope of 1.5 (see red dashed line). The linear approximation is quite accurate for rods having an aspect ratio larger than 5.

Figure 2.5: Resonance wavelength of a gold ellipsoid having both short axes equal to 40 nm in an air environment (n=1). The resonance is shown in function of the long axis length of the rod according to the Mie-Gans theory (black curve). A linear dependency with a slope of 1.5 (red curve) is noticeable for rods having an aspect ratio larger than 5.

2.3 Coupled nanoparticles

When two metallic particles come in close proximity to each other, the electric field in the vicinity of one particle is expressed as a sum of the incident electric field and of the field generated by the other particle. This results in an energy splitting in a bonding and antibonding state as it can be seen in Figure 2.6 [NOP+04]. The lowest energy state corresponds
2.4 Damping mechanisms in plasmon resonance

Scattering events due to impurities, phonons and other electrons with the collective oscillation of the electrons in metals perturbate the phase coherence of the resonance. The behavior of the electron can be compared with a damped harmonic oscillator described by Equation 2.10

$$\ddot{z} + \gamma \dot{z} + \omega_0^2 z = f_0 \exp(i\omega t)$$ (2.10)

which has a resonance at $\sqrt{\omega_0^2 - \gamma^2}$ with a half width at half maximum (FWHM) of $2\gamma$. The dephasing time $\tau$ can be defined by $1/\gamma$ and can be thus retrieved from the FWHM from the measurement. Typical values for the dephasing time are found between 3 fs – 20 fs for different nanostructures [BYT+13, SFW+02]. The corresponding FWHM for different resonance wavelengths and dephasing times is shown in Figure 2.7.

Figure 2.6: Plasmon hybridization in interacting nanoparticles leading to a splitting of the energy level in a bonding and anti-bonding state. The colors and signs correspond to the electrical density in the rods at resonance.

to the bonding state which is equivalent to the dipole bright mode. The difference in energy between the uncoupled mode ($E_2$) and the bonding mode ($E_1$) is proportional to the gap size [HKG+10]. A larger gap size will thus reduce the energy of the system leading to a red shift of the resonance. A detailed derivation of the mode frequency can be found in [MRFPS+08]. The anti-bonding mode don’t posses a net dipole moment and do not scatter to the far field. For this reason they are offen refered as dark modes [GTA+13, DFDB+12].
2.5 Quantum versus classical field theory

Optical antennas are in the range of ten to several hundreds of nanometers formed by several thousands to millions of atoms. In a first thought we can describe their interaction with light with a classical model. Optical antennas are usually formed by dimers separated by small gap sizes of the order of 1 – 20 nm where phonons can potentially tunnel through the gap in this region.

It was demonstrated experimentally that the quantum limit is reached only for gap sizes smaller than half a nanometer [SHE+ 12]. The simulation of plasmonic antennas with classical electrodynamics can thus be considered for antennas having gaps larger than this values.
2.6 Wavelength scaling and optical antennas

Antennas are widely used in the radio frequency regime and their design makes use of structures with characteristic length $L$ that are directly related to the wavelength $\lambda$ of the incoming radiation. One of the widely used designs is half-wavelength dipole antennas made of thin rods of length $L = \frac{1}{2} \cdot \lambda$. However at optical frequencies the simple wavelength scaling breaks down because the incident radiation is no longer perfectly reflected from a metal surface. Instead, radiation penetrates into the metal and gives rise to oscillations of the free-electron gas [Nov07].

Figure 2.8 shows the effective wavelength ($\lambda_{\text{eff}}$) for gold rods as demonstrated in [Nov07]. The rods have their ending rounded by a radius $R$. For example a half-wave antenna made of a gold rod with a length of 135 nm ($\lambda_{\text{eff}} = 270$ nm) which correspond to an external wavelength of 670, 860 and 1240 nm for an antenna having a rounding radius of 20, 10 and 5 nm respectively.

![Figure 2.8: Effective wavelength for circular gold rods. The curves are calculated according to [Nov07], where $R$ is the wire radius of the antenna. The rods are surrounded by vacuum ($\varepsilon = 1$).](image-url)
CHAPTER 2. THEORETICAL BACKGROUND AND SIMULATIONS

2.7 Simulation

Because analytical solutions for the resonance frequencies can be derived only for a small number of very simple particle shapes, numerical methods must be used for the design and analysis of more complex geometries.

Various methods such as the finite difference time domain (FDTD) method [ON04], the finite element method (FEM) [HNVD10], the boundary element method (BEM) [GdAH98], the T-matrix approach [MVB+04], the discrete dipole approximation (DDA) [YH07], the generalized multiparticle Mie (GMM) theory [IX95], the multiple multipole method (MMP) [HB83, SVH09], and more have been employed for this purpose. Each method has its own advantages and disadvantages.

FEM has several advantages compared to other methods. FEM may use a tetrahedral meshes or even curved elements which avoids stair-casing effects that are typical for FDTD. According to Taflove [TH05], plasmonic structures require an extremely fine grid of 0.5 nm or less in order to perform accurate FDTD simulations. This require a large amount of memory and computational time. The presence of a substrate can be included relatively easily with FEM, which is typically not the case with BEM and MMP which have problems with boundaries where more than two domains intersect. One of the big disadvantages of FEM is the need for meshing the whole environment around the structure of interest which increases drastically the memory consumption and the computational time.

In the frame of this thesis we performed FEM simulations with the commercially available software COMSOL MULTIPHYSICS. We started using the version 4.3a with the RF module in 3D solved for the frequency domain. We discovered that this version has a major issue when using perfectly matched layers (PML) in the $x$-axis and we thus upgraded our software to version 4.3b. All presented simulations were performed with COMSOL 4.3b.

2.7.1 Geometries

We simulated mainly dipole and bowtie antennas with different parameters for the geometry, such as antenna length, gap size, thickness, etc.
**Dipole antenna**

Figure 2.9(a) and 2.9(b) show the top and side views of the geometry used with the default values used in the simulation, if not explicitly specified. The dipole antennas consist of a pair of two metallic rods separated by a specific gap, having a thickness $T$ and a width $W$ which had typical values of 20 nm and 45 nm respectively. The total length $L_{\text{tot}}$ was defined as the span length between the two extremities of the antenna including the gap. It has a default value of 130 nm. The two extremities of the antenna where rounded with a diameter which is equal to the width of the antenna arm in order to mimic the obtained geometry after fabrication. All of the other edges where rounded with a radius $r_o$ of 5 nm in order to avoid divergence of the electric field in the simulations and to match the geometry achieved by the fabrication process.

![Figure 2.9: Geometry of dipole antennas as used in the simulations.](image)

**Bowtie antenna**

The geometry of the bowtie antenna is basically formed by a pair of extruded and smoothed triangles. The construction of such an antenna is explained in Figure 2.10, where the antenna
Figure 2.10: Schematic explanation of the geometry construction process for bowtie antennas. (a) 2D creation of the smoothed triangle by boolean union of 3 circles and one polygon. (b) Extrusion of the triangle to the target thickness minus the smoothing radius $r_o$. (c) Extrusion of another triangle with the same center and smaller in size by $2r_o$ and to the target thickness. (d) The smoothed corners of the edges are created with torus sections. (e) The smoothed edges are created by cylinders. (f) Everything is boolean summed to an antenna arm or a full antenna for simulation performed on non-symmetric structures or illuminations.

is formed by a triangle with smoothed corners and extruded to obtain the thickness of the antenna. The edges and corners at the top of the antenna were smoother in order to have more realistic structures compared to what can be fabricated. This also avoids any divergence of the electric field during the simulations.

Originaly bowtie antennas were introduced to supplement dipole antenna in order to achieve a higher bandwidth required for telecommunication applications such as television. For the case of plasmonic bowtie antennas, the bandwidth is quite comparable to dipole antennas. Here three main interests are for this geometry. First, they have sharp apex in their gap leading to a high electric field enhancement and thus a better sensitivity. Second, we believe that
the stretching of bridged (gapless) bowtie antennas can break in their narrowest region to form very small gap sizes. Third, they have a larger surface which can be required for fabrication reasons as it will be discussed in Chapter 5.

Antennas fabricated with a low dose during the electron beam lithography step (see Chapter 3) can also become concave and in extreme cases so skinny that they form three branches looking like a star (see Figure 2.11). Such antennas were also investigated by simulations.

The trigonometrical calculations used for the design of the bowtie antennas are summarized in Appendix B.

Figure 2.11: Different geometries used in simulations for bowtie antennas.

2.7.2 Boundary Conditions

3D simulations are highly time consuming and require a lot of memory. In order to increase the computational efficiency, one can take advantage of the symmetries of the antenna and model only one quarter of the required volume. As depicted in Figure 2.9, the system has two planes of symmetry. The first one lies perpendicular to the axis of the antenna and perpendicular to the substrate. In the case of a $0^\circ$ polarization, in regards to the antenna axis, the electric field has to be perpendicular to this plane and this condition can be fulfilled with a perfect electric conductor (PEC). The second symmetry lies along the axis of the antenna and perpendicular to the substrate. In the case of a $0^\circ$ polarization the magnetic field has to be perpendicular to this plane and this condition can be fulfilled with a perfect magnetic conductor (PMC). With this technique we can use a quarter of the memory and also shorten
drastically the computational time. With this simplification only a planewave illumination parallel to the substrate with a polarization angle of either 0° or 90° with regard to the long axis of the antenna can be used. If one wants to simulate structures illuminated with a specific angle, the symmetry is broken and the technique described above cannot be directly applied. The most efficient way to handle this consists in a symmetry decomposition of the incident wave and separate solution of each symmetry component. Essentially, a Fourier series in $\phi$ direction is performed, where $\phi$ is the angular direction around the axis of the structure. COMSOL cannot automatically perform such a Fourier decomposition and we solved the problem by simulating the entire volume without using a PEC and a PMC boundary condition.

In this thesis we focused mainly on plane waves which are perpendicularly incident to the substrate with the polarization parallel to the axis of the antenna if not specified otherwise. Simulation studies with different polarizations and incident angles are presented at the end of this chapter.

2.7.3 Material

For the simulations we used different materials which are summarized in Table 2.1. The substrate was either glass or PDMS. As different glasses were used in the fabrication process we used a refractive index which was wavelength independently set to 1.5 for the simulations. This simplification gives an error of about 2% for the refractive index. For the case of PDMS a wavelength independent value of 1.4 was used. With this simplification we face an error of 1%. Sometimes a thin layer (2 nm) of titanium was deposited in order to avoid charging during the whole fabrication process. This layer oxidizes quickly and was modeled with the Sellmeier equation (see Table 2.1) as the wavelength dependency varies about 20% in the visible. If not specified the environment was set to be air with a refractive index of 1.

2.7.4 Mesh

The meshing is a very important task in FEM simulation and has to be chosen carefully. If the mesh is too coarse the simulation won’t be accurate and field artifacts might occur such as unwanted reflections. However, if the mesh is too fine, the simulation will take more computational time and memory. The computers we used for the simulations have a limited amount of ram (32 Gb or 24 Gb depending on the computer) which implies that the total number of
### Table 2.1: Material and parameters used in the simulations.

<table>
<thead>
<tr>
<th>Material</th>
<th>Wavelength dependency &amp; Parameters</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>$n = 1, k = 0, \forall \lambda$</td>
<td>-</td>
</tr>
<tr>
<td>Glass</td>
<td>$n = 1.5, k = 0, \forall \lambda$</td>
<td>-</td>
</tr>
<tr>
<td>Gold</td>
<td>Interpolation from empirical values</td>
<td>[JC72]</td>
</tr>
<tr>
<td>TiO2</td>
<td>Sellmeier: $n^2 = 5.913 + \frac{0.2441}{\lambda^2 - 0.0803 \mu m^2}$</td>
<td>[DeV51]</td>
</tr>
<tr>
<td>PDMS</td>
<td>$n = 1.4, k = 0, \forall \lambda$</td>
<td>-</td>
</tr>
<tr>
<td>PMMA</td>
<td>$n = 1.5, k = 0, \forall \lambda$</td>
<td>-</td>
</tr>
</tbody>
</table>

Meshing elements has to be constrained. The electric field far away from the structure is usually very close to the value given by the excitation field, meaning that the relative field intensity is very low and does not change drastically over space. For this reason a coarse mesh might be used at the boundary of the computational domain. As the metallic structure creates a lot of scattering and all of the electric field is confined in the vicinity of the antenna a very fine mesh has to be used in this region.

The example of the resulting mesh of the antenna can be seen in Figure 2.12. The detail of the meshing strategy used is described in Figure 2.13.

![Figure 2.12: Mesh used for the antenna simulations.](image)

#### 2.7.5 Scattered field intensity

The COMSOL simulation software solves the given problem for the electric field using the various solvers. We used the direct solver PARDISO [SG04] which is more robust than the iterative
Figure 2.13: Meshing strategy used in Comsol. All meshing elements were either triangular or tetrahedral.
In the case of optical antennas we are interested in the scattering properties of the antenna. This property should be measured in the far field. COMSOL has an internal function to calculate the far field in function of the computed near field. In reality this technique is only accurate when the boundary is homogeneous and cannot be applied when a substrate is present.

One way to approximate the far field is to integrate the scattered Poynting vector which is normal to the surface on a sphere around the antenna. This should be integrated far away from the structure of interest. As measurements will be performed by collecting the light with a microscope objective under the substrate, the scattering intensity will be integrated only over half of the sphere. In reality this is an approximation as microscope objectives have a limited numerical aperture (NA) and collect only a smaller solid angle.

\[
I_{\text{scat}} = \int_{\Gamma_r} \mathbf{S}_{\text{scat}} \cdot \mathbf{n} \, ds
\]  

where \( \mathbf{n} \) is the normal vector and \( \Gamma_r \) the half-sphere of radius \( r \):

\[
\Gamma_r = \{ \mathbf{x} \in \mathbb{R}^3 \mid |\mathbf{x}| = r \text{ and } x_3 < 0 \}
\]  

and \( \mathbf{S}_{\text{scat}} \) the Poynting vector of the scattered field which is defined in COMSOL as the “relative time-average power outflow”.

On the one hand, the sphere radius should be large enough so that the near field of the antenna does not have any influence, but on the other hand the sphere should not be too close to the PML layer in order to avoid artifacts and errors from the non perfect implementation of the PML as it will be demonstrated at the end of this chapter. It finally means that a compromise of the computational domain size should be done in order to avoid errors and to keep the number of meshing elements below the memory (RAM) limit. We chose a PML radius of 500 nm which correspond to half of the maximum simulated wavelength. As we investigated plasmonic antennas with a maximum arm length of 200 nm and as the near field decays exponentially, we set the integration sphere \((\Gamma_r^-)\) radius to \( r = 400 \text{ nm} \).

### 2.7.6 Incident electromagnetic field

Each simulation provides the scattering intensity of an optical antenna excited with a specific incoming wave. In a multilayer system, as used in this thesis, where the environment consist-
ing of an adhesion layer and a substrate are modeled, the excitation cannot be provided by 
the boundary condition in an efficient way. The easiest and most accurate solution is to solve 
the problem for scattered fields. In this way, the excitation can be introduced by defining a 
background electric field $E_0$. The total electric field $E_{\text{tot}}$ can then be split in the background field and the scattered field $E_{\text{scat}}$, i.e.: $E_{\text{tot}} = E_0 + E_{\text{scat}}$

This approach has several advantages. The first one is to be still accurate even if $E_{\text{scat}}$ is much larger than $E_0$ which is the case in the vicinity of the antenna gap where the field enhancement is large. The second advantage is that it allows to describe the excitation through the background field. $E_0$ can be derived from a simulation performed only with the substrate, but without the optical antenna, in order to calculate the propagation of the incoming wave described by a boundary condition. This method is one of the easiest, but is also time consuming as each simulation for each wavelength and each antenna geometry has to be performed twice. Third, the FEM solutions are never perfect and always subject to numerical errors due to the meshing. Reusing the solution of a previous simulation as the initial value can lead to error propagation and higher inaccuracy of the final solution.

A method to reduce computation time and minimize the errors is to calculate the electric field value of the incoming wave analytically. This can easily be done for three layers using the Fabry-Perot derivation. The appendix A shows the details of this calculation.

The efficiency of this method can be tested by performing simulations without any antenna, but just with the 3-layer system. We performed those tests with refractive indices of 1, 1.5 and 1.4 (from top to bottom), corresponding to the media of air, PMMA and PDMS. We modeled the whole computational domain here in order to perform simulations with illuminations having various incident angles.

The results of the theoretically simulated electric field presented above are shown for the $s$- and $p$-polarization in Figures 2.14 and 2.15 respectively for an incident electric field norm equal to 1. The deviation of the simulated results of the computational domain without antenna and the theoretical calculation given as input is typically as low as $5 \cdot 10^{-6}$ for the $x$- and $y$-component of the electric field as it can be seen on figures 2.14(b), 2.14(c), 2.15(b) and 2.15(c). A larger deviation of the order of 2% was measured for the $z$-component of the electric field for the $s$-polarization as well as for the $p$-polarization having an incoming angle of $0^\circ$ (see figures 2.14(d) and 2.15(d)). These artifacts most likely come from simulation inaccuracies coming from bad absorption of the PML and cannot be easily corrected$^1$.

---

$^1$It is not excluded that future version of COMSOL provides a better implementation for the PML reducing those inaccuracies.
2.7. SIMULATION

(a) $x$-component of the electric field for an $s$-polarized wave with an angle of $0^\circ$.

(b) $x$-component of the difference between the simulated electric field and the theory for an $s$-polarized wave with an angle of $0^\circ$.

(c) $y$-component of the electric field for an $s$-polarized wave with an angle of $0^\circ$.

(d) $z$-component of the electric field for an $s$-polarized wave with an angle of $0^\circ$.

(e) $x$-component of the electric field for an $s$-polarized wave with an angle of $30^\circ$.

(f) $x$-component of the electric field for an $s$-polarized wave with an angle of $60^\circ$.

Figure 2.14: Simulation results for the electric field of an $s$-polarized (along the $x$-axis) wave incident from the top with an angle of $0^\circ$, $30^\circ$ and $60^\circ$. The simulation errors are in the order of $5 \cdot 10^{-6}$ for the $x$- and $y$-components of the electrical field and reach nearly 2% for the $z$-component. All plots display the $yz$ plane at $x = 0$ for an illumination wavelength of 700 nm.
CHAPTER 2. THEORETICAL BACKGROUND AND SIMULATIONS

(a) $x$-component of the electric field for a $p$-polarized wave with an angle of $0^\circ$.

(b) $x$-component of the difference between the simulated electric field and the theory for a $p$-polarized wave with an angle of $0^\circ$.

(c) $y$-component of the electric field for a $p$-polarized wave with an angle of $0^\circ$.

(d) $z$-component of the electric field for a $p$-polarized wave with an angle of $0^\circ$.

(e) $x$-component of the electric field for a $p$-polarized wave with an angle of $30^\circ$.

(f) $z$-component of the electric field for a $p$-polarized wave with an angle of $30^\circ$.

Figure 2.15: Simulation results for the electric field of a $p$-polarized (in x/z-axis) wave incident from the top with an angle between $0$ and $30^\circ$. The simulation errors are in the order of $5 \cdot 10^{-6}$ for the $x$- and $y$-components of the electrical field and reach nearly 2% for the $z$-component when the incident angle is zero. Plots (a-d) display the y/z plane at $x = 0$ and the x/z plane at $y = 0$ for the plots (e-f). The shown results were simulated with a free space wavelength of 700 nm.
**Illumination angle relation**

For an $s$-polarized wave along the long axis of the antenna ($x$-axis), the illumination angle does not change the $x$-component of the electric field (see Figure 2.16(d)). This means that changing the incident angle of an $s$-polarized wave will not change the resonance wavelength of the antenna; only the coupling efficiency with the antenna and thus the intensity of the scattered spectra will be affected. Then it can be expected to observe the same spectra with higher incident angle, but with a smaller intensity. This was confirmed by our simulations as it can be seen in Figure 2.16(a). For the case of a $p$-polarized wave along the $x$-axis, the projection of the electric field along the $x, y$ and $z$ axis change with the incident angle (see Figure 2.16(d)). This introduces changes in the response behavior of the antenna as it can be seen in Figure 2.16(b).

**Polarization angle**

The polarization angle will define which mode of the antenna will be excited. With a polarization along the long axis of the antenna, the dipolar bright mode will be excited which is one of the strongest due to the presence of the small gap. As shown in Figure 2.16(c), the $90^\circ$ polarization will excite another mode, which is blue shifted, but also less strong, for a 300 nm bowtie antenna having a 10 nm gap size. Once an antenna is measured or simulated for the $0^\circ$ and $90^\circ$ polarization, all the other polarizations can easily be deduced from this result. An electric field with a polarization angle $\phi$, can be written as

$$E(\phi) \propto \begin{pmatrix} \cos \phi \\ \sin \phi \\ 0 \end{pmatrix}$$

The intensity which is proportional to the square of the electric field norm becomes

$$I \propto |E|^2 \propto \cos^2 \phi + \sin^2 \phi$$

This means that the scattering intensity of an antenna with polarization $\phi$ is

$$I_{\text{scat}}(\phi) I_0 \cos^2 \phi + I_{90} \sin^2 \phi$$
where $I_0$ and $I_{90}$ are the scattering intensities corresponding to the 0° and 90° polarization, respectively. This was verified by our simulation as it can be seen on Figure 2.16(c), where the polarization was swept between a polarization angle of 0° and 90°.

Figure 2.16: Simulation on bowtie antennas having a total length of 300 nm and a gap size of 10 nm. The illumination was polarized along the long axis of the antenna with different incident angles.
2.8 Conclusions

We have demonstrated that using the theoretically derived field for the illumination through the substrate with the FEM software COMSOL MULTIPHYSICS give rise to some artifacts close to the PML. The calculation of the far field effectuated by integrating the Poynting vector projection on a sphere far away to the structure, but not too close to the PML in order to avoid the previously mentioned artifacts is a good solution to estimate the scattering spectra of nanostructures. We believe that this simulation method is adequate for plasmonic application, but a good care should be taken to the black box status of commercial software and every steps of the simulations should be tested and verified carefully.
Chapter 3

Methods

One of the main tasks in this thesis was the fabrication of diverse plasmonic antenna geometries on different substrate materials. Two important challenges were the fabrication of dipole antennas with a sub-5nm gap size and the ability to produce bowtie antennas on a flexible substrate. In this chapter all the fabrication and characterization methods used in the frame of this thesis are presented.

3.1 Materials

In the following paragraph the different materials used for the fabrication and simulation of optical antennas are presented in details.

3.1.1 Metal for the plasmonic antennas

The antenna itself requires to be metallic in order to allow plasmon oscillations. Different metals present different suitability for plasmonic applications. Table 3.1 summarize the plasmonic ability of various metals. If one takes also into account the chemical stability of the material and its biocompatibility, gold remains as the best choice for plasmonic applications. In the frame of this thesis, the metal used for the plasmonic antennas was exclusively gold. Nevertheless all the fabrication techniques used and described here can be slightly adapted when working with other materials.
CHAPTER 3. METHODS

Table 3.1: Comparison of the suitability of different metals for plasmonic applications [RCZ+11].

<table>
<thead>
<tr>
<th>Metal</th>
<th>plasmonic ability</th>
<th>chemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum (Al)</td>
<td>good in UV region</td>
<td>stable after surface passivation</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>interband transitions below 600 nm</td>
<td>easy oxidation</td>
</tr>
<tr>
<td>Gold (Au)</td>
<td>interband transitions below 500 nm</td>
<td>very stable, high quality factor</td>
</tr>
<tr>
<td></td>
<td></td>
<td>biocompatible</td>
</tr>
<tr>
<td>Palladium (Pd)</td>
<td>low quality factor, not suitable for plasmonics</td>
<td>stable</td>
</tr>
<tr>
<td>Platinum (Pt)</td>
<td>low quality factor, not suitable for plasmonics</td>
<td>stable</td>
</tr>
<tr>
<td>Silver (Ag)</td>
<td>highest quality factor</td>
<td>oxidation, biocompatibility issues</td>
</tr>
</tbody>
</table>

3.1.2 Substrate

The substrate should be a dielectric and has to be transparent in order to perform optical measurements in transmission. For the case of a hard substrate, both glass and fused silica fulfill these requirements and present the additional advantage of being cheap, flat and of good optical quality after cleaning.

In this thesis the fabrication of plasmonic structures on a flexible substrate was also demonstrated and investigated. The material used as a flexible substrate should be transparent, chemically stable and preferably resistant to solvents and high temperature. We thus focused on polydimethylsiloxane (PDMS) which fulfills all these requirements. PDMS has also the advantage of being biocompatible and very popular in the fabrication of microfluidic channels. These properties eventually will facilitate the integration of optical antennas as a sensor into more complex device such as in microfluidic channels or Lab-on-a-chip. The polymer atomic configuration of PDMS can be seen in Figure 3.1. The PDMS used in this thesis was exclusively from a SYLGARD 184 kit from DOW CORNING and was mixed with a ratio of 1:10 in weight with the curing agent. The mixture was steered thoroughly for 1–2 minutes and then defoamed in vacuum in a desiccator for about 30 minutes. After this, the PDMS was poured and then cured at room temperature for at least 48 hours. We observed that curing PDMS at higher temperature decreases the polymerization time which also decreases the polymer-chain length and results in a more fragile rubber which can break more easily even at low strain.
3.2 Fabrication

The fabrication process of a plasmonic antenna starts with a clean substrate to which a pattern of the desired material is transferred. This section describes in detail how each step was performed. However, the recipes used for the fabrication of optical antennas will be discussed in the individual chapters.

3.2.1 Cleaning

Fabrication of nanostructures requires clean and flat surfaces in order to minimize the presence of dust and impurities which would induce defects in the fabricated structures. Each sample was cleaned thoroughly for 5 minutes with ultrasonic agitation in an acetone bath, then in an isopropanol (IPA) one and finally rinsed in deionized water (DI-water). The samples were then dried with a nitrogen gun. Commercial glasses were also pre-cleaned with water and soap, then rinsed with DI-water followed by the cleaning procedure described above. Each sample was inspected by eye to check the optical quality of the substrate and re-cleaned if needed.

PDMS samples were not cleaned as they are poured from the clean liquid phase directly onto the structures. Moreover, PDMS swells solvents and is water repellent which renders efficient cleaning difficult. A special care of PDMS should be taken during storage of samples in order to avoid contamination from the ambient air.

3.2.2 Pattern transfer

In the following, the different techniques used in the fabrication of structures in the frame of this thesis are described. The techniques exploited and experimented are electron beam lithography (EBL), Gallium focused ion beam milling (Ga-FIB) and Helium focused ion beam milling (He-FIB). In Table 3.2 the different properties of these techniques as well as there
advantages are summarized.

Table 3.2: Pro and cons of electron beam lithography (EBL), Ga focused ion beam (FIB) and He FIB for pattern transfer of nanostructures.

<table>
<thead>
<tr>
<th></th>
<th>EBL</th>
<th>Ga-FIB</th>
<th>He-FIB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum structure size</td>
<td>10nm</td>
<td>20nm</td>
<td>3.5nm</td>
</tr>
<tr>
<td>Contamination</td>
<td>low</td>
<td>high</td>
<td>average</td>
</tr>
<tr>
<td>Speed</td>
<td>average</td>
<td>slow</td>
<td>slow (milling) / average (exposure$^b$)</td>
</tr>
<tr>
<td>Possibility to mill large area?</td>
<td>✓</td>
<td>✓</td>
<td>✗</td>
</tr>
<tr>
<td>Need a mask (resist)?</td>
<td>✓</td>
<td>✗</td>
<td>✗ (milling) / ✓ (exposure)</td>
</tr>
</tbody>
</table>

$^a$The given sizes are typical values which are easily achieved. Nevertheless smaller structure sizes can be achieved in special cases.

$^b$exposure of resist as in lithography technique.

3.2.3 Pattern transfer by Electron Beam Lithography

Electron beam lithography (EBL) is perhaps the most popular way to produce nanostructures of various kinds, because the electron beam can be focused down to a nanometer size and can be scanned to define custom patterns. In reality, however, the resolution is reduced at best to $\approx 2$ nm for isolated structures and $\approx 5$ nm for dense structures in the resist [MZS$^+13$] and is further reduced to $\approx 10$ nm after the pattern is transferred from resist to gold antennas [JD13, KM10]. All the reported values above were achieved on thin (10–30 nm) silicon nitride membranes. The disadvantage of membranes is that they are very fragile and have limited size. In case of bulk substrates the lithography is limited to $\approx 10$ nm due to an effect of back scattered electrons during the EBL step [HSLB04]. After the pattern transfer the antennas are reliably fabricated with gap sizes down to 15–20 nm [ZFSM09].

In the frame of this thesis all EBL exposures were performed on a RAITH150-TWO system. The interaction volume of the electrons in the resist limits the achievable resolution. In order to obtain a high resolution, two different approaches exist. The first one is to use high energy (30 keV) electrons on a thin substrate, such as a 30 nm thick silicon nitride membrane. In this configuration there are very few back scattered electrons and most of the primary electrons go through the membrane leading to a very small beam-resist interaction volume. The second approach is to reduce the primary beam energy to 5 keV in order to reduce the interaction volume and thus increase the resolution as explained by the empirical formula 3.1 [KO72], where $R$ is the interaction radius (in $\mu$m), $A$ the atomic weight (in g/mole), $\rho$ the density (in g · cm$^3$), $E_0$ the incident beam energy (in keV) and $Z$ the atomic number of the substrate.
This last technique has the advantage to be applicable on every substrate type. Nevertheless special caution should be observed for non-conductive samples. Those will be charged during the exposure and can lead to drifts as demonstrated in Figure 3.2(a) which shows the result after EBL was performed on a fused silica substrate without any conducting layer. Straight lines are distorted, the resolution of the structures is decreased and the position of the beam might be shifted a lot and overlaps with already exposed structures. In order to overcome this problem a thin conductive layer can be deposited either on the top or on the bottom of the resist. Good results were obtained with 50 nm of copper (Cu) below the resist, but this implies that the fabricated structures will also sit on this layer which is problematic for plasmonic applications. The second method is to deposit 5 nm of Cu on top of the resist. The Cu can be removed after exposure with a mixture of HNO₃ 1:10 H₂O for 2 minutes before the development of the resist. This has the disadvantage to use a different dose in order to expose the resist and to decrease the fabrication resolution as the electrons have to penetrate through the Cu layer. Figure 3.2(b) shows the result after lift-off of a bowtie antenna exposed to EBL with 5 nm of Cu on top of the resist. We see that the antenna has quite a few defects which are due to the presence of the non-homogeneous Cu layer.

\[
R = \frac{2.76 \cdot 10^{-2} A \rho^{5/3}}{Z^{8/9}} \cdot \rho
\]  

(3.1)
CHAPTER 3. METHODS

Resist spinning

For EBL a 50 nm thick PMMA layer was spun on the samples as a resist. In order to achieve a high resolution a single layer having a thickness of 50 nm was targeted. In order to avoid any problem during the lift-off process the range 50–55 nm was chosen. Tests with different PMMA concentration in ethyl-lactate (EL) was tested on glass substrate (see Figure 3.3). PMMA 2:3 in EL spun at 3 krpm seems to be the best choice in order to achieve a resist thickness of 50 nm.

![Spin curve of PMMA 950k with different dilutions in ethyl lactate (EL), spun for 40 s and baked for 300 s at 180°C. PMMA 950k 2:3 EL spun at 3 krpm fit the target thickness of 50–55 nm (gray box) the best. Except for PMMA 950k in 1:1 EL which was performed only on one sample per speed, the other measurements are displayed in the box plot format which display the median (thick line in the box), the upper and lower quartile are represented by the box (see [Ben88] for more details about the box plot).](image1)

Patterning on flexible substrate

Unfortunately the patterning of flexible substrates, such as PDMS, was found to be impossible after some trials. The main problem is that PDMS expands with temperature, humidity, vacuum and swells in contact with solvents such as acetone and IPA. This expansion and relaxation of the rubber creates cracks in the deposited films on the PDMS such as the resist.
For this reason we weren’t able to perform any direct patterning of structures on top of the PDMS with EBL.

The solution we found is to perform the patterning of the structures on a hard substrate and then to transfer them onto PDMS. Chapter 5 gives more detail about this technique.

### 3.2.4 Patterning data

The patterning is done by scanning the beam over the area of interest. Large structures are usually obtained by scanning the area defined by its borders. This usually gives nice shape results and only the size should be scaled to obtained the dimension of interest for a given development time and exposure dose. For smaller structures, scanning the entire area deteriorates the obtained geometry due to the Gaussian beam shape. One solution is to approximate the desired shape by a superposition of lines. For the case of dipole antennas (two rods), single pixel lines where used with different doses to tune the width of the antenna. Figure 3.4(a) displays the obtained antenna width, measured on SEM images, in function of the line dose used during single pixel line exposure. We see that the obtained width for the same antenna might vary up to ±5 nm between the left and right arm of each antenna (see Figure 3.4(b)).

![Figure 3.4](image_url)

(a) Width as a function of the line dose used. (b) Asymmetry between the right and left arm of each dipole antenna.

**Figure 3.4:** Dipole antenna width after 20 nm of gold lift-off on a Silicon substrate spun with a 50 nm PMMA resist. Each antenna was exposed at 5 kV with a single pixel line for each arm.

For the case of bowtie antennas three main patterning methods were used depending on the target size of the antennas. First, antennas having a total size larger than 400 nm were
patterned by scanning the full area of two triangles. Second, for antennas having a size larger than 250 nm and smaller than 400 nm, the triangles of each arm were scanned by a series of horizontal lines as shown in Figure 3.5(a). In order to avoid roughness at the two vertical outer edges, two vertical lines are used to obtain smooth edges. The spacing used between the lines ($d$ in Figure 3.5(a)) was 5 nm. Third, for antennas having a total length smaller than 250 nm, the patterning was obtained by using a set of three lines per arm forming a star shape as shown by the red lines in Figure 3.5(b). With a high enough dose, the three branches of the stars merge together and form a triangular shape which tends to be concave for low dose and convex for higher ones. The green areas in Figure 3.5(b) display the exposition levels which correspond to the effective dose received by the sample due to the Gaussian shape of the beam. For a fixed development time, this corresponds to the obtained shapes for the different line doses employed, where small doses will result in shapes depicted in light green and high dose in shapes shown in dark green. SEM images of such antennas are displayed in Figure 3.6 where doses between $250 - 1200 \text{pA} \cdot \text{cm}^{-1}$ were used.

Figure 3.5: Schematic representation of the pattern used to fabricate bowtie antennas by electron beam lithography. (a) Pattern using a set of lines for bowties having a size larger than 250 nm. (b) Pattern using three lines forming a star (see red lines) for bowties having a full span length smaller than 250 nm. The different colors show the results obtained using different doses (light color correspond to low dose).

The pattern generators used in both EBL and FIB systems are from RAI TH company and can read GDS data files. Structures can be created by hand with the provided RAI TH software which is time consuming and subject to mistakes. In order to improve the design of the structure we developed a script to automatically create the patterns for the structures in GDS file format. This developed library is freely accessible under the GNU GPL license under https://github.com/scholi/libgds.
3.2.5 Resist development

Once the structures have been exposed to the e-beam, they should be developed in order to remove the exposed part of the resist. Usually PMMA is developed in methyl isobutyl ketone (MIBK) 1:3 isopropanol for 30 seconds. In the case of fabrication of very small structures it is a big advantage to reach a development with a high contrast. It was demonstrated that development in pure isopropanol results in an enhancement of the contrast [WLK07]. For this reason we developed every sample in pure isopropanol for 5 minutes. The development time was kept constant and the dose was adjusted in order to obtain structures of the desired size and shape (see Figure 3.6).

![Figure 3.6: Results after lift-off of bowtie antenna patterned with three star shaped lines per antenna arm using different doses. The substrate was silicon and the antennas are made out of 20 nm of gold. (a) Star antenna patterned with a low dose (typically around 250 pAs·cm⁻¹). (b) Star antenna patterned with a medium dose (typically around 800 pAs·cm⁻¹). (c) Star antenna patterned with a high dose (typically around 1200 pAs·cm⁻¹).](image)

3.2.6 Pattern transfer by gallium focused ion beam

Focused ion beam (FIB) techniques use beams of ions which are accelerated and deflected in order to remove material on specific locations of the sample. This technique is quite convenient as it does not require a mask or a resist in order to pattern the substrate. As opposed to EBL, FIB is a negative technique as it removes material where the beam is focused. It can thus become challenging to fabricate isolated structures with this technique.

In order to fabricate optical antennas, first a thin layer of gold is evaporated on top of the desired substrate. The thickness of the film determines the thickness of the antennas. The material around the antenna has to be milled away by FIB. This has two main disadvantages. The first one is that in order to achieve isolated structures, a very large area around the struc-
ture of interest has to be milled away. This step is time consuming and will implement a lot of Ga atoms into the substrate. Moreover, this will disconnect the structure from the ground and leave it surrounded by a large non-conductive area resulting in charging and drifts during the milling process. Drifts decrease the achievable resolution and can damage the structures. The second disadvantage is that the gold has to be completely milled away and an over-milling is usually necessary as polycrystalline gold has a different sputtering yield for different crystal orientation. This will result in a different over-milling depth into the substrate and will lead to a non-flat surface which will contribute to scattering from the background. Those problems were verified and are demonstrated in the following two sections.

Fabrication of optical antennas on hard substrates

Fabrication of optical antennas on a hard substrate by Ga-FIB was demonstrated to be reliable. Figures 3.7(a) and 3.7(b) demonstrate the fabrication of bowtie antennas having a total size of 800 nm with gaps in the range of 30–50 nm or gapless. We were not able to fabricate antennas with gaps in the sub-20 nm range by Ga-FIB due to its low resolution capability. This means that EBL remains the best fabrication tool in order to fabricate optical antennas on a hard substrate accurately and in a reproducible way. Ga-FIB also has the big disadvantage to implement Ga atoms into the substrate which alter the effective refractive index, and thus the optical response of the antenna, in a non-controllable way.

Fabrication of optical antennas on flexible substrate

The patterning of structures by EBL on flexible substrate, such as PDMS, was not possible due to the swelling of solvents by the substrate (see section 3.2.3). As FIB milling is a direct process, requiring no mask and no resist, we tested its capability in fabricating optical antennas on PDMS. The results of dipole antennas milled by Ga-FIB are shown in Figure 3.7(c) and 3.7(d). We see that it’s hard to achieve a complete removal of the gold around the antenna. Drifts seem to occur and leave specific spots of the substrate untouched. Over-milling is thus required, but, as can be seen in Figure 3.7(c), this induces a lot of cracks in the structure itself due to drift. Drifts arise probably due to charging, because PDMS is non-conductive and the antenna becomes electrically isolated from the rest of the gold film as the milling progresses. Only one antenna could be fabricated in a satisfactory way (see Figure 3.8(a)). We were unable to reproduce it afterward. Most of the time drifts occur creating cracks and gold deformation (see Figure 3.8(b)). By optimizing the dose and the number of loops during the
3.2. FABRICATION

Figure 3.7: SEM images of Ga-FIB milled bowtie (a&b) and dipole (c&d) antennas in a 20 nm thick Au layer. Substrates were Si (a&b) and PDMS (c&d). Bowtie antennas had a total length of 800 nm. Where hard substrate gives satisfactory results, PDMS shows high drift and large inhomogeneities in the milling rate. (a) Results for antennas with gaps in the range 30–50 nm. (b) Results for gapless antenna. (c) Crack formation during the milling of isolated rods. (d) Milling of an isolated rod. The obtained size was $548 \times 144$ nm.

milling we were able to optimize the obtained result. But the fabricated structures are not very reproducible as it can be seen in Figure 3.8(c) where four antennas were milled with the exact same parameters giving four different results.

Due to all these problems, Ga-FIB milling was not retained for the fabrication of optical an-
tennas on PDMS as it leads to too irreproducible results.

Figure 3.8: SEM images of Ga-FIB milled bowtie antennas on a 20 nm thick gold layer deposited onto PDMS. The milling process shows a lot of deformations coming from the substrate which results in cracks, asymmetries and inhomogeneities of the antennas. All the milling was performed with a current of 30 pA. Milling performed with: (a)&(c) a dose of $100 \mu C \cdot cm^{-2}$ and 100 loops, (b) a dose of $25 \mu C \cdot cm^{-2}$ and 200 loops.
3.2.7 Pattern transfer by Helium focused ion beam

He focused ion beam (He-FIB) is similar to Ga-FIB except that ionized He atoms are used instead of Ga. As the mass and size of He atom is much smaller than Ga, a higher resolution in the fabrication is achievable. On the other hand, and for the same reason, the milling time is much longer.

As the sputter yield of Au atoms by He ions with an energy of 30 keV is about 0.13 [ea83, YT96], a lot of helium ions are implanted into the substrate. If the diffusion rate is lower than the milling current, accumulation of the helium ions will occur in the sample and the milling process will stop (I. Shorubalko, unpublished). For this reason only a small area can be milled and optical antennas cannot be fabricated directly from a continuous gold film.

In order to achieve isolated optical antennas, rods of the desired dimension can be produced by another fabrication technique such as electron beam lithography. The rods can then be cut by focused He-ion beam in order to achieve very narrow gap sizes (see chapter 4).

Scotch tape lithography

In order to create isolated structures without the need to combine the He-FIB milling with another fabrication tool, as explained in the last section, one can mill only the outline of the structure and remove the gold surrounding the structures by a lift-off technique. This lift-off can be performed by taping a piece of scotch on top of the sample and to strip it away. The continuous gold film will stick to the tape and be removed from the sample. As the structures are too small to have a good adhesion to the tape, they will stay on the sample. Figure 3.9 shows the result of bowtie antenna milling by He-FIB on a 30 nm thick gold film deposited by Ar sputtering on a PDMS film. Antennas with large gaps are easily achieved by milling two triangles (Figure 3.9(a)). In order to obtain a small gap, the easiest way is to first produce an antenna with a bridge (Figure 3.9(b)) and then open the gap with a single pixel line milling (Figure 3.9(c)).

Unfortunately for us, the lift-off process didn't work as expected. Part of the gold around the antennas also stuck to the substrate and was not lifted-off. A He-FIB image of a milled array of antennas is shown in Figure 3.9(e). White spots show the changes of the material present in the interaction volume with the ions. An optical microscope image after tape lift-off of the same array is visible in Figure 3.9(f). We see that the whole frame around the antennas wasn't lifted-off. This is most probably due to the interaction of the ions and electrons with...
Figure 3.9: Outline milling of bowtie antennas by He-FIB in a gold film deposited onto a PDMS substrate (a–d). (a) A gap is automatically created due to the proximity effect of the beam. (b) Gapless antenna milling. (c) Gapless antenna can be opened by an additional milled line in order to reach low gap antennas. (d) High quality antennas can be performed only with a good alignment of the beam. Here stigmatization problems is shown where asymmetry is visible between the two edges which are oriented SW-NE compared to the ones NW-SE. (e) The contamination and redeposition by He-FIB is clearly visible in this array of milled bowties One antenna is present in the middle of each white spot. (f) Optical image after the Scotch lift-off step. The image shows the same spot as (e). We see that the whole frame around the antennas array is not lifted-off and the same shadows as the ones present in (e) are visible. (g) SEM image after tape lift-off on an antenna array which was not imaged before lift-off. (h) SEM image zoom on one of the antenna shown in (g).
the substrate which enhances the adhesion properties resulting in the impossibility to lift-off correctly the exposed area around the structures. In the example shown in Figure 3.9(e)-(f) the frame was imaged with the He-FIB before lift-off, but even when the structures are created blindly, i.e. no imaging was performed between FIB milling and lift-off, the procedure was not successful. Results of such structures after lift-off are shown in Figure 3.9(g) and (h). Here no imaging frame is visible, but we see that the area around each antenna which is in the interaction volume with the incoming ions sticks on the substrate.

This technique has been demonstrated to work on large structures created by evaporating gold on a patterned substrate [CPP+13]. The group of Prof. Leiderer (Universität Konstanz) were able to achieve a tape lift-off of structures by milling their outline by Ga-FIB (known through personal communication; unpublished) as long as the structures are not imaged by FIB or SEM before the lift-off. Unfortunately we demonstrated that this lift-off technique cannot be applied on structures milled by He-FIB. The reason is that He-FIB, due to its lower sputter yield, produces much more secondary electrons (SE) compared to Ga-FIB. Those SE will contribute to the binding enhancement of the gold to the substrate and thus avoid a proper lift-off.

### 3.2.8 Metal deposition

All the metals we used in the fabrication process were deposited by electron beam physical vapor deposition (EBPVD). The machine used was a Plassys-II MEB 500 equipped mainly with Ti, Cu, Au and Cr. The deposition thickness was controlled by a quartz oscillator. The deposition was performed with rotation for homogeneous films and without rotation for the metals used during the lift-off process to avoid them to stick at the border of the resist during evaporation. Multiple metal layers can be evaporated without venting the machine. Thus, oxidizing of the titanium (Ti) adhesion layer, deposited between the gold and the substrate material, can be avoided.

### 3.2.9 Antenna fabrication with controlled defects

We had the ambition to create and characterize optical antennas with different kinds of defects in order to understand their role better and in order to predict their impact. This would allow to include fabrication defects in the design of optical antennas and to reach more reliable results. We fabricated antennas with two types of defects. Either antennas with tailings
as depicted in Figure 3.10 (last image of the right column) or with undercuts (last image of the left column). The idea is to exploit the Gaussian shape of the electron beam used for the lithography steps.

Figure 3.10: Two fabrication processes to create dipole antennas with different kinds of undercuts. The first technique (displayed on the right column) uses traditional e-beam lithography with gold evaporation and lift-off process in order to produce antennas with small tails due to the beam shape which interacts with the resist. The second technique (left column) uses a negative resist in order to create antennas with undercuts. In order to avoid gold to stick to the resist border, traditional lift-off process cannot be used and here an electroplating step is required. As electroplating only works on conductive materials, a thin gold layer was deposited below the resist.

For the case of antennas with tailings, the fabrication process is comparable to what was already discussed previously in the EBL section (3.2.3). A PMMA 950k resist is spun onto glass, then a thin Cu layer is evaporated in order to avoid charging during exposure. After Cu removal and development, gold is evaporated and the resist is lifted-off in acetone. This results in antennas with small tailings (see right column of Figure 3.10).
For the case of antennas with undercuts, the fabrication process is different (see Figure 3.10 left column). First a thin conductive layer is evaporated. For our first test gold was used. Then a negative resist (AR-N7700.18 2:7 in AZ) was spun at 4 krpm for 40 s and baked at 85°C for 60 s. EBL was performed, but instead of exposing the antenna area, the negative structures were exposed (ie. everything except the structure; similar to FIB). After EBL, the samples were baked at 100°C for 300 s in order to create the cross-link. Samples were then developed in AR 300-47 for 120 s. Here lift-off cannot be used, otherwise the evaporated gold would stick to the resist and the lift-off process would remove all the gold leaving no structures at all. In order to overcome this problem we used an electroplating step which requires a conductive layer. This explains why for this process the conductive layer was evaporated below the resist and not on top of it. After electroplating, the resist was stripped off in acetone.

Unfortunately the fabricated structures using electroplating on a negative resist was not reliable as shown in Figure 3.11. First, these antennas present a lot of undesired defects. Second, the area between antennas shows a high roughness and strange patterns which might disturb the characterization. As here the visualization of those defects are under the antenna, the exact geometry cannot be measured with techniques such as atomic force microscopy (AFM) or SEM. Moreover our optical characterization tool is an aperture scanning near-field optical microscope (SNOM) which can reach a resolution of at best of 50 nm. This is not enough to study those small defects in detail. For those reasons the fabrication of optical antennas with undercut defects was put aside and we will concentrate on the fabrication of optical antennas with a positive resist.

![SEM image of dipole antennas created by electroplating gold on a negative resist.](image-url)
3.3 Characterization

The characterization of the produced antennas consists of two steps. First the obtained geometry should be investigated which is usually done by either a scanning electron microscope (SEM) or by an atomic force microscope (AFM). Second, the optical properties of the antennas can be investigated by spectroscopy measurements.

3.3.1 Scanning Electron Microscopy

One of the first properties of the antennas which should be characterized are their geometries. One of the easiest and quickest methods is probably to produce an image using a scanning electron microscope (SEM). The two different SEMs used in the frame of this thesis are:

**Hitachi S-4800** which uses a cold field emission. Images presented in this thesis obtained with this tool have the label "EMPA" written in the bottom left part of the image.

**Zeiss ULTRA 55** Images presented in this thesis obtained with this tool have the logo "Zeiss" written in the bottom right part of the image.

3.3.2 Atomic Force Microscopy

Atomic force microscopy (AFM) was performed on an ASYLM RESEARCH AFM using probes working in non-contact mode.

3.3.3 Spectroscopy

Scattering spectras were acquired with an Olympus IX-81 inverted microscope with one of its output coupled to an Andor Shamrock 301i monochromator equipped with an iDUS DV420A camera. The microscope is equipped with a 10X and a 60X objective (see table 3.3 for details). The detector has a size of $1024 \times 254$ pixels$^2$. When the monochromator has its entry slit widely opened (2.5 mm), it has a field of view of $638 \times 203 \mu \text{m}^2$ and $104 \times 32 \mu \text{m}^2$ for the 10X and 60X objective respectively. Spectras were acquired with a slit opening of 150 $\mu\text{m}$ which corresponds to 1.9 $\mu\text{m}$ for the 60X objective. This is large enough to collect the whole spectrum emitted by a single antenna.
Table 3.3: List of the objectives used in the IX-81 microscope

<table>
<thead>
<tr>
<th>Objective</th>
<th>Name</th>
<th>NA</th>
</tr>
</thead>
<tbody>
<tr>
<td>10X</td>
<td>Olympus Plan C N</td>
<td>0.25</td>
</tr>
<tr>
<td>60X</td>
<td>Olympus LUCPlanFLN</td>
<td>0.7</td>
</tr>
</tbody>
</table>

The illumination source is a tungsten-halogen lamp with its internal IR filter removed in order to perform measurements in the near-IR (NIR). The measured spectra of the source is shown in Figure 3.12(a). The quick drop in the NIR is due to the low quantum efficiency (QE) of the detector in this spectral region.

![Image](image.png)

**Figure 3.12:** (a) Spectrum of the halogen lamp (red curve) without any corrections for the optical components of the spectrometer. The drop of the intensity above 700 nm is due to the low quantum efficiency (QE) of the detector in this region (see blue curve). (b) Schematic of the setup used for spectroscopy.

**Calibration**

Our spectrometer has a Czerny-Turner configuration as shown in Figure 3.13.

The core of the spectrometer is a grating placed in the middle which can be rotated. Incoming light with an angle $\alpha$ on a grating will be reflected with an angle $\beta$ when the following...
CHAPTER 3. METHODS

Figure 3.13: Schematic of a spectrometer in the Czerny-Turner configuration. The deviation angle \( D = \beta - \alpha \) is constant and depends on the spectrometer. The grating can be rotated to an angle \( \phi = \beta + \alpha \). This will change the central wavelength. The resolution of the obtained spectra depends on the groove spacing \( d \).

condition is fulfilled:

\[
m \lambda = d (\sin \alpha + \sin \beta)
\]

where \( m \) in an integer representing the reflexion order, \( d \) the groove spacing of the grating and \( \lambda \) the wavelength of light. In a spectrometer the deviation angle \( D = \beta - \alpha \) between the incident and the diffracted direction remains constant. The grating can be rotated to the scan angle \( \phi = \alpha + \beta \). Equation 3.2 can be simplified for the first order (\( m = 1 \)) to

\[
\lambda_0 = 2d \cos \frac{D}{2} \sin \frac{\phi}{2}
\]

Thus the grating can be rotated in order to choose the center wavelength \( \lambda_0 \) that the camera will detect at its central pixel. The 0° degree can be calibrated using the entry slit, set to a small opening width such that the image of the slit hits the detector at its central pixel. For a specific scan angle \( \phi \) the wavelength dispersion on the camera can be fitted using a third order polynomial. This polynomial is easily calibrated with a light source having several sharp peaks such as with fluorescent light. Peaks of this commercial light come from transitions of Mercury, Argon, Terbium and Europium which are present in the lamp tube and can be fitted according to an online database [oSN]. The spectrum of our calibration lamp recorded with our spectrometer is displayed in Figure 3.14. We see that after calibration all theoretical
Figure 3.14: Spectra of the fluorescent light used for calibration of the spectrometer. The wavelengths written on top of the peaks are provided from the online database [oSN].

values (displayed by text and red lines) match well with our measurement. An error of 0.5 nm is a typical value for the grating we are using (150 lines · mm⁻¹).

Scattering spectrum measurement

The scattering spectrum measurement of an object can be performed easily in dark field (DF). In DF the illumination hits the sample only with high angles which are not collected by the objective due to the small numerical aperture (NA). For instance the dry 60X objective has a NA of 0.7. This means that the minimum illumination angle for the DF is \(\arcsin 0.7 \approx 44^\circ\).

The measured spectrum depends on many different factors such as:

- lamp spectrum (and thus lamp temperature and voltage used)
- optical elements in the microscope (lenses, mirrors)
- polarizer
- Spectrometer optics (2 mirrors)
• Grating efficiency of the spectrometer

• Quantum efficiency of the camera

The true scattering spectra can be calculated by compensating for all those effects. A spectrum \( S_{a,DF}(\lambda) \) can be measured in DF on an antenna, then the scattering coming from the substrate \( S_{0,DF} \) can be measured next to the antenna and finally the spectrum in bright field (BF) can be measured on the substrate \( (S_{bg,BF}) \). Even if the camera was cooled down to \(-70^\circ\text{C}\), it still has some dark current, which was measured \( (S_x) \) with the same integration time as for the real measurement \( (S_x) \). The scattering spectrum of the antenna can then be calculated with Equation 3.4.

\[
S(\lambda) = \left( S_{a,DF}(\lambda) - S_{a,DF}(\lambda) \right) - \left( S_{0,DF}(\lambda) - S_{0,DF}(\lambda) \right) \]

\[
S_{bg,BF}(\lambda) - S_{bg,BF}(\lambda)
\]

In the nominator of the equation, the scattering coming from the substrate is subtracted and in the denominator we compensate the spectrum for the lamp, the grating efficiency, the detector efficiency and all the optical components (mirrors, polarizators, etc.). One should note that as soon as \( S_{bg,BF}(\lambda) \) approaches zero, the result will diverge and be very noisy. This is the case for wavelengths with low QE of the detector (above 1000 nm) and for frequencies for which the lamp has a low emission (below 500 nm).

Figure 3.15 shows the image of an antenna array with its label under the microscope (figure 3.15(a)), and the same antenna seen by the spectrometer with its entry slit wide open and its grating tilted to 0° (Figure 3.15(b)). Figure 3.15(c) shows the image obtained by the spectrometer when its entry slit is open to 150 \( \mu \text{m} \). We see that this slit opening is wide enough to collect the scattering spectrum of the whole antenna.
Figure 3.15: Image of bowtie antennas taken by the optical microscope and the spectrometer with its grating tilted to $0^\circ$. The spectrometer takes images only in black and white. They are thus presented here in false color. **(a)** Image taken by the IX81 microscope in dark-field with a 60X objective. **(b)** Image of the same structures as shown in (a) recorded by the spectrometer. The image is rotated $90^\circ$ clockwise and flipped vertically due to mirrors between the microscope and the spectrometer. **(c)** Example of antennas aligned in the spectrometer slit. Here the slit width was $150\mu m$. 
Chapter 4

Dipole antennas with sub 5-nm gap

This chapter presents a fabrication method to produce dipole antennas with a gap size in the sub-5 nm range and the characterization of those antennas. This study was published in a slightly modified version with the following reference: O. Scholder, K. Jefimovs, I. Shorubalko, Ch. Hafner, U. Sennhauser and G-L. Bona: “Helium Focused Ion Beam Fabricated Plasmonic Antennas with sub-5 nm Gaps”, *Nanotechnology*, 24, 2013.

4.1 Introduction

Dipole antennas are one of the easiest and most studied type in the antenna theory. As already discussed in the Section 3.2.3 optical antenna can be fabricated by EBL with a gap size in the range of 15 – 20 nm reproducibly. A method to produce antennas down to 3 nm by a two step lithography process with defining an oxidized mask between the steps was recently demonstrated [ZBW+11]. However, this method is limited to a single gap value per substrate.

He-FIB milling is a new and very promising technique which became recently commercially available [SSN+08]. It was found that this instrument has a high potential for nanostructuring at the 5 nm level by direct milling of the material. However the sputter rate of a He-FIB is much lower than the one of a Ga-FIB as He ions have a much lower mass. In this thesis, we demonstrate a simple and robust way to produce plasmonic dipole antennas with gaps down to 3.5 nm by combining electron beam lithography and helium focused ion beam milling. While the EBL was used to produce single gold rods, He milling was used to cut them in half and to reproducibly define gaps in a range from 20 nm down to 3.5 nm with a reproducibility of about 1 nm.
4.2 Methods

4.2.1 Fabrication

The fabrication process of plasmonic antennas is schematically illustrated in Figure 4.1. We used a standard microscopy glass cover slip (borosilicate D 263 M, Schott) as a substrate (Figure 4.1(a)). A 2 nm titanium layer was deposited by electron beam physical vapor deposition (EBPVD) in order to avoid charging during the following EBL and He-FIB steps (Figure 4.1(b)). A 50 nm layer of PMMA 950k (Allresist GmbH) was used as a resist (Figure 4.1(c)). The EBL step was performed with a RAITH 150TWO system using a beam energy of 5 kV and a current of 18 pA (Figure 4.1(d)). Rods were created using single-pixel line exposure with a length of 100 nm, a step size of 1 nm and a line dose of 500 pC cm\(^{-1}\). The sample was developed for 5 minutes in pure isopropanol at room temperature. After development a 2 nm titanium adhesion layer and 20 nm gold were deposited by EBPVD (Figure 4.1(e)). Lift-off was performed in acetone using ultrasonic agitation (Figure 4.1(f)). This process resulted in elliptically shaped gold islands of about 50 \(\times\) 130 nm\(^2\) in size. Gaps of the plasmonic antennas were produced by direct milling with focused He ions using a CARL ZEISS SMT ORION PLUS helium ion microscope (Figure 4.1(g)). We used a beam energy of 30 keV, a beam current of \(\approx\) 1 pA and a step size of 1 nm for milling. We varied gap sizes by defining different widths of the milled area. Depending on the width of the milled area we adjusted the dose by varying the dwell time (40 – 700 \(\mu\)s) and number of loops (50 to 100).

![Fabrication of plasmonic dipole antennas by EBL and He-FIB milling.](image)

**Figure 4.1:** Fabrication of plasmonic dipole antennas by EBL and He-FIB milling.
For more information about the fabrication, the details of the procedures are discussed in Chapter 3.

### 4.3 Results & Discussion

He-microscope images of fabricated plasmonic antennas are shown in Figure 4.2. The top row shows the nanostructures produced by EBL and lift-off. The rectangles over the structures correspond to the areas to be milled by He-FIB. The bottom row shows the results after cutting the gaps by He-FIB with the gap value measured from the image.

**Figure 4.2:** Helium microscope images of the structures. **Top**) Image after electron beam lithography step. The rectangles over the structures correspond to the area to be milled by helium focused ion beam (He-FIB). **Bottom**) Image of the same structures after the He-FIB milling. The values in the images are the measured gap sizes. All scale bars are 50 nm.

The He-microscope images shown in Figure 4.2 are based on secondary electrons (SE) produced by He ions. The gap was defined as a full width at half maximum (FWHM) of the SE-signal, obtained from the cross section through the antenna (see Figure 4.3). The width of the SE images taken with He-microscopy is 300 nm with a resolution of 512 pixels. Thus, the pixel size is 0.586 nm giving an accuracy of the measurement for the gap of \( \approx 1.2 \text{ nm} \) (one pixel on each side). A higher zoom would result in a larger degradation of the antenna through the imaging process. The minimum gap achieved was 3.5 nm, which corresponds to milling using a single pixel scan with a current of 0.9 pA, a dwell time of 200 \( \mu \text{s} \) and 50 loops (see Figure 4.3).

We fabricated antennas of different gap sizes by adjusting the dwell time \( \tau \), the beam current \( I \), the nominal (milled) width and the number of loops \( N \). The FWHM of the gap of antennas as a function of the milled width is shown in Figure 4.4. A width of 1 nm corresponds to a
CHAPTER 4. DIPOLE ANTENNAS WITH SUB 5-NM GAP

Figure 4.3: Measurements of the produced gap sizes, defined at the full width at half maximum (FWHM) of the secondary electron (SE) signal in the cross section through the antenna in the vicinity of the gap. The He-microscope image and a green rectangle, where the cross section of the SE-signal is taken is shown in the lower inset. The SE-signal of the cross section through the complete antenna is shown in the upper inset.

Figure 4.4: The FWHM of the obtained gap size as a function of the nominal width used for the milled area. The gaps milled with different doses are shown with different colors. Sample 1 was milled with a wide range of gap sizes, from single pixel line (1 nm) to 20 nm while sample 2 was focused on reproducibility of gap sizes between 1 and 5 nm.
single pixel line scan with focused helium ions. Different colors in the plot correspond to different doses, which were calculated according to Equation 4.1, where $sz$ is the step size.

$$\text{dose} = \tau \cdot N \cdot I \cdot sz^{-2}$$ (4.1)

One can see that for gaps above 10 nm the width of the gaps is well matching the width of the milled area. For the smaller lines the obtained width tends to saturate at about 5 nm. This is caused by the physical limitation of the sputtering process with helium ions at this energy [ASF+11]. With a careful adjustment of the dose we were able to get some antennas with a smaller gap. However, the gap values there do strongly depend on the dose. Also the images do not provide information whether the antennas are cut all the way through the 20 nm thick gold layer due to the high aspect ratio of the produced trench; the optical response of antennas with lowest gaps indicates that this is likely the case. One of the main limiting factors for reproducible gap milling in this range is the stability of the system during the milling time, as even a tiny drift may eventually cause a widening of the milled lines, which explains a slight spreading of the obtained gap. As example the scattering spectra measurements of the antenna presented in Figure 4.2 are shown in Figure 4.5.

![Resonance curves of dipole antennas milled by He-FIB](image)

**Figure 4.5:** Resonance curves of dipole antennas milled by He-FIB. Each curves correspond to the spectra of the antennas presented in Figure 4.2 with the corresponding color.

In the case of gaps larger than 5 nm, the resonance wavelength of the measurements matches well with the simulations (see Figure 4.5 and 4.6). Simulations were performed for a perfect
geometry, a homogeneous material and a wavelength step of 10 nm (see Chapter 2 for details). In reality the fabricated antenna suffer from defects, mostly related to the material inhomogeneities due to the polycrystalline structure of gold. These nanocrystals have different crystal orientation, grain sizes and form roughness both in lateral and vertical directions. The deviations from perfection add an extra damping, which broadens the measured resonance. Nevertheless, the resonance position is in good agreement with the measurements.

![Resonance of an antenna with a 10 nm gap size compared to simulation. The inset show the geometry used for the simulations. The intensities were scaled to have a unit values at their peak for both the measurements and the simulations.](image)

**Figure 4.6:** Resonance of an antenna with a 10 nm gap size compared to simulation. The inset show the geometry used for the simulations. The intensities were scaled to have a unit values at their peak for both the measurements and the simulations.

In order to compare the performance of antennas we show the resonance wavelength (Figure 4.7(a)) and a relative scattering intensity at resonance (Figure 4.7(b)) as a function of the measured gap size of the antennas. One can clearly see a red shift of the resonance wavelength and an increase of the scattering intensity of antennas when reducing the gap size. The simulation results show good agreement with measurements. However, the experimentally measured resonances for smaller gap sizes are spectrally more red shifted, compared to simulations. This can be caused by several factors.

First, the ion milling process is always associated with a certain degree of redeposition of the sputtered material. This redeposition loads the antenna with a dielectric material and thus shifts its resonance wavelength toward the red. As the spectral sensitivity of the plasmonic antennas is higher for smaller gap sizes [FM08], one can expect a stronger spectral shift due
4.3. RESULTS & DISCUSSION

![Graphs showing resonance wavelength and intensity as a function of gap size for samples 1 and 2, along with simulations for different refractive indices.](image)

**Figure 4.7:** Optical response of plasmonic antennas with different gap sizes. (a) Resonance wavelength of the antennas as a function of their gap size. Simulations are performed for two different refractive indices of the environment: 1 and 1.5 (corresponding to values of air and glass, resp.). The gray area shown around the simulation curve is the uncertainty of the resonance wavelength. (b) Relative scattering intensity of the antennas as a function of their gap size. The measurements show a good agreement with the simulations.

Second, we have to note here that the curves of Figure 4.4 and 4.7(a) contain measurements from two different samples. They were milled using a different length of the cut rectangles - 70 nm for sample 1 and 100 nm for sample 2. One can assume that as this causes more substrate milling for sample 2, it would result in a stronger redeposition effect of dielectric material onto the antenna, especially in the vicinity of the gap and into the gap itself. This argument is supported by observing a larger (on average) red shift of the resonance wavelength for antennas of sample 2 (blue circles) compared to sample 1 (red circles).

### 4.3.1 Refractive index sensing

To confirm the refractive index sensing capability of He-FIB fabricated antennas, we performed spectral measurements of the samples in water. For this, we put a drop of water onto the substrate and covered it with a 250 µm thick glass cover slip. This allowed us to prevent the water from evaporating and to keep the water layer on the sample flat, which avoids light dis-
Figure 4.8: Refractive index sensitivity. (a) Resonance wavelength as a function of antenna gap size measured in air and water. (b) Resonance Shift per refractive index unit (RIU) for antenna having different gap sizes.

tortions. The measurements are summarized in Figure 4.8. Different colors correspond to the resonance wavelength of the antennas when the sample is in air (red) and water (blue). Circles and triangles correspond to measurements of sample 1 and 2, respectively. The dashed curves are simulation results. We can see a clear red shift for all the antennas within a gap size range of 3.5 to 21 nm. The shift of the plasmonic resonances in units of nanometer per refractive index unit (nm/RIU) as a function of antenna gap size when the sample is immersed in water is plotted in Figure 4.8(b). The wavelength shift is about 100 nm/RIU for gap sizes above 5 nm and increases to values of about 250 nm/RIU for gap sizes smaller than 5 nm.

Simulations on the resonance wavelength of the antenna were performed with different refractive index values for the environment (see Figure 4.9). The calculated points (open circles) are fitted by a straight line in order to define the sensitivity of the antenna. The sensitivities of antennas are defined as the slope of the straight lines in units of nanometers per refractive index unit (nm/RIU) and are marked above the lines, corresponding to antennas with different gaps. As shown, the sensitivity increases with decreasing the gap size.
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Figure 4.9: Resonance wavelength as a function of the refractive index of the environment for antennas with a different gap sizes. Sensitivity values are written on top of each fitting lines in units of nm/RIU.

4.3.2 Bridged antennas

The difference between the measurements and the simulations are especially large for small gap sizes (see Figure 4.7(a)). Dipole antennas with small gaps also correspond to a small milling dose. As a result, this means that these antennas might not be cut completely through for low dose, leaving the dipole with a small bridge connecting its two arms. For this purpose we have simulated such bridged antennas. Their geometry is identical to normal antennas with gaps, except that a small gold cylinder bridges the gap as it can be seen in Figure 4.10. In order to avoid any singularities, the cylinder is smoothed at its connecting region with the antenna arm.

The results show a clear blue shift which is in good agreement with simulations performed by others [LWZ+13]. This blue shift can also be explained due to the presence of a negative dielectric and thus this induces a shift of the resonance wavelength which goes in the opposite direction compared to dielectrics. As we observed a redshift compared to our simulation instead of a blue one, we expect that even antennas with small gaps are not connected.
4.3.3 Tapered gap geometry

An other explanation of the difference between the measurement and our simulations is the gap geometry which is not a perfect plate capacitor. In reality milling by FIB creates beveled trenches due to the Gaussian shape of the beam. This results in a non homogeneous gap size with a smaller value at its bottom toward the substrate and a larger one at the top of the gap (see top image of Figure 4.11(a)).

Simulations performed for a tapered gap having a bottom size of 2 nm and a top size of 8 nm show very similar result as antennas with a vertical gap having a size of 2 nm (see Figure 4.11(a) and (b)). We notice that the electric field is concentrated towards the bottom of the antenna in the narrow gap region (see Figure 4.11(c)).

Our measurement of the gap size was performed by taking the FWHM directly from the secondary electron (SE) image obtained by the He-FIB. The rounded edges at the top of the gap release a lot of SE which give a good image contrast. This means that the measured gap size is closer to the top value than the bottom one. The high aspect ratio of the antenna (thickness compared to its gap size) is too large to be measured with AFM. He-FIB imaging performed...
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Figure 4.11: Simulation of antennas with different gap sizes and shapes. (a) Geometries and gap sizes used for the simulations. The frame color correspond to the curves color displayed in (b). (b) Simulations of the scattering spectra. (c) Norm of the electric field of 5 planes parallel to the substrate for a V-shaped gap. The illumination had a wavelength of 790 nm.

at a higher magnification will, at the same time, mill the observed area and thus modify its geometry.

4.3.4 Redeposition

A third aspect to be taken into account when comparing the simulated and measured results is the redeposition of material which occurs during the milling process. The He-FIB removes material from the antenna and the substrate. This material is partly redeposited in the vicinity of the milled area and changes slightly the effective refractive index in the vicinity of the gap. As the electric field reaches its highest value in the gap, changes of its refractive index in this region will also have a higher impact on the resonance of the antenna. As observed by our simulations and measurements (see Figure 4.8(b)) we see that antennas are more sensitive to environmental changes for small gaps leading to a higher wavelength shift for small gap sizes.

We performed simulations for four different cases which are illustrated in Figure 4.12(a). The first one is the standard perfect antenna which sits on a thin Ti layer on a glass substrate (gold frame). Second we have simulated the case of an antenna completely embedded into glass (green frame). Third we simulated antennas coated with a titanium oxide shell (red frame).
Last we simulated antennas coated with a Glass shell (blue frame). In all cases we observe a red shift which is in agreement with other simulations of antennas loaded with dielectric material [LWZ+13].

4.3.5 Antenna reshaping

He-FIB milling also allows us to reshape the antenna before opening the gap. One example of this reshaping is shown on Figure 4.13, where a gold rod (a) was reshaped to an antenna with rectangular arms as shown in (b). Spectra of such antennas are very similar to the non-reshaped ones for an equivalent gap size (see Figure 4.14(a)). By comparing the wavelength resonance of the antenna in function of its gap size (see Figure 4.14(b)) we notice that very small differences are visible compared to the non-reshaped ones. Reshaped antennas are slightly shorter and should have a resonance wavelength slightly blue-shifted compared to non-reshaped ones. This blueshift was also verified by our simulations as it can be seen in Figure 4.14(b). Our measurements are quite scattered, but still the resonance wavelengths of reshaped antennas are slightly blue shifted compared to the non-reshaped ones for gaps larger than 7 nm. The higher scattering of the measurements for reshaped antennas can
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Figure 4.13: (a) He-FIB image of an obtained gold rod after lithography. (b) He-FIB image of the same rod as shown in (a) after arm reshaping and gap opening by He-FIB. The pattern used for reshaping is still visible on the image as a slight overmilling altered the titanium layer.

be explained by uncontrolled formation of asymmetries and defects in the antenna which can change drastically the antenna response. Such asymmetries are visible in Figure 4.13(b) where the top right corners of each arm are slightly different from the other corners. As the milled area is larger than the structure, the conductive layer is milled away around the antenna leaving it disconnected from the ground and thus more subject to charging problems during the milling process. Charging of the sample will create drifts during milling which are mainly responsible of the defects and asymmetries formation of the antenna.

For small gap size the electric field is concentrated in the gap and thus less sensitive to defects present in the corners of the antenna. This effect is visible by the lower scattering of the measurements data for gap sizes smaller than 7 nm. In this gap range the antennas also don’t show big differences in the resonance wavelength between reshaped and non-reshaped antennas and no blueshift is visible.

In the case of reshaping, the substrate is more heavily milled, which creates higher redeposition compared to the case of non–reshaped antennas. As discussed before, the redeposition might create loading of the antenna or more generally the formation of a dielectric shell layer around the antenna which induces a redshift. This redshift might compensate the blueshift due to the smaller antenna length resulting in the same behavior as non–reshaped antennas.
CHAPTER 4. DIPOLE ANTENNAS WITH SUB 5-NM GAP

(a) Spectra of five reshaped antennas having different gaps sizes (see legend). Each measurement is fitted by a Lorentzian (gray curve) and its resonance wavelength is displayed by a dashed vertical line and its value in nm. The antenna A3 is the one displayed on Figure 4.13(b).

Figure 4.14: Spectra of reshaped dipole antennas by He-FIB milling. Spectra of individual antennas having the same length but with different gaps are presented.

4.4 Conclusion

In conclusion, we have demonstrated a robust process for the fabrication of plasmonic gold dipole antennas by cutting gaps with widths of 3.5 – 20 nm in a controllable and reproducible way with a precision of ≈ 1 nm by helium ion milling. Scattering spectra of the antennas reveal an increase of the intensity and a red shift of the peak of the scattered light with a decrease of the gap size. The difference of measured plasmonic resonances for the smallest gap compared to the simulations is explained by redeposition of the substrate material and by conservative definition of the gap size at FWHM, as the size at the bottom of the gap has a smaller width due to the sloped sidewalls. We have measured an increase of the sensitivity of antennas with smaller gap sizes, up to values of ≈ 250 nm/RIU. We believe that the demonstrated technology to produce plasmonic antennas with He-FIB will find its applications in biosensing, Raman analysis and optical communications.
Chapter 5

Bowtie antennas with tunable gap

5.1 Introduction

Typically optical antennas have a geometry which is fixed during the fabrication process and thus an optical response which depends only on their environment. This property can be exploited for biosensing applications where a small change in the environment, such as the presence of molecules in the vicinity of the antenna changes its resonance wavelength.

Resonance of optical antennas have a typical full width at half maximum (FWHM) in the order of 100 nm (see Chapter 4 and the results section of this chapter). If one is interested in performing measurements in different regions of the spectrum, several antennas having different resonance wavelengths should be fabricated on the same sample in order to cover the whole spectral range of interest. Fabrication processes at the scale of the nanometer is not perfectly reliable and often lead to the implementation of defects or result in a slightly different geometry as the designed one. For those reasons a large set of optical antennas with various sizes should be fabricated in order to cover the spectral area of interest.

As discussed in Chapter 4 the resonance wavelength of an antenna can be tuned by varying its gap size and keeping the rest of its geometry fixed. If an antenna is deposited on a flexible substrate, its gap size can be mechanically tuned by stretching the substrate along the long axis of the antenna. The basic principle is depicted in Figure 5.1, where the gap sizes are increased by applying a strain to the substrate. In the case of an antenna deposited directly on flexible rubber (Figure 5.1(a)), the gap size can be increased only proportionally to its gap size at rest. Smaller gap sizes are characterized by a higher measurement sensitivity, but result in a lower tunability. For instance an antenna having a gap of 5 nm deposited on a
CHAPTER 5. BOWTIE ANTENNAS WITH TUNABLE GAP

Flexible substrate which is stretched by a strain of 10% can have its gap size tuned up to only 5.5 nm (ie. an increase of also 10%). Moreover the strain of the substrate will be transferred partly to the arms of the antenna which will either become longer or slip on the surface in order to release the strain accumulated into the arms of the antenna. In the first case the geometry of the antenna will be changed and in the second the antenna gap size will change uncontrollably as the slipping mechanism can occur either towards the gap or in the other direction depending on where the adhesion between the antenna and the substrate is the highest.

As the metal of the antenna is, in our case, evaporated gold which forms grains, the strain accumulated in the gold film might create cracks in order to release the strain as shown in Figure 5.1(b). Cracks change the conductivity of the metallic arms which will result in a drastic change on the optical properties of the antenna.

One of the solutions to avoid cracks and increase the tunability is displayed in Figure 5.1(c), where the antenna is mounted on pillars. Here the stretching capability will be drastically enhanced, because the effective gap stretching will occur on a larger length than the gap size size of the antenna (see dashed lines). The presence of posts will also relax the strain in the substrate avoiding crack formations in the antenna. With this method the antenna stretching

Figure 5.1: Stretching mechanism of an optical antenna. (a) In the case of an antenna deposited directly on a flexible substrate the gap tuning will be very limited. (b) Due to the grain structure of the metal which forms the antenna, the stretching might create cracks along the antenna in order to release the strain which builds up in the metal. In this figure cracks are exaggerated for clarity. (c) Antenna deposited on pillars. Here the gap tunability is enhanced and less cracks should appear in the antenna arms as the pillars (green) should reduce the stress in the metal film. (d) Spectral shift of the resonance wavelength of an antenna. The red curve displays a typical resonance behavior of an antenna. The blue curve shows the response of the same antenna when the substrate is stretched. Here the stretching increases its gap size and thus its resonance wavelength will be blue shifted.
5.2 Fabrication methods

Fabrication of bowtie antennas on PDMS can be achieved by electron beam lithography (EBL), but unfortunately a direct patterning on the PDMS is not possible. EBL requires a development and a lift-off step in solvents (typically acetone and isopropanol). However, these solvents are swelled by the PDMS [LPW03], which avoid the steps to be executed correctly. One solution is to pattern the bowtie antennas on a hard substrate and then transfer them onto PDMS. The adhesion between PDMS and gold is quite low, and a direct pouring of the PDMS onto the structures followed by striping off the PDMS film was unsuccessful.

We also tried to spin a thin layer of (3-mercaptopropyl)trimethoxysilane (MPTS) on top of the structures before pouring the PDMS. MPTS has two different functional groups: one thiol
and three methoxy (as seen in red and green respectively in Figure 5.2). The thiol group is usually used in self-assembly systems because it sticks easily to gold [OLL+09]. On the other side, the methoxy group sticks more easily to organic materials such as PDMS. We expected that this molecule would improve the adhesion between the gold antennas and the PDMS substrate.

![Chemical formula of (3-mercaptopropyl)trimethoxysilane (MPTS). It has two functional groups. A thiol (red) which binds easily with gold and three methoxy (green) which bind easily with polymers.](image)

Unfortunately this step didn’t improve the adhesion of gold to the PDMS sufficiently to allow a successful transfer of the antennas.

Even if this method would have worked it would have remained problematic as the PDMS has to be peeled, and thus bent, in order to be stripped off. Bending of the film deforms the surface and can introduce defects into the structures, such as cracks, which can lead to a drastic change and decrease of the optical properties of the structures.

We developed a new technique in order to transfer patterns from a hard substrate onto PDMS which is summarized in Figure 5.3. First a conductive layer of copper (Cu) is evaporated by electron beam physical vapor deposition (EBPVD) on a glass substrate (Figure 5.3(a) & (b)). The sample is rotated with a speed of 4 rpm during the evaporation in order to obtain a homogeneous film. One of the main roles of this Cu layer is to prevent charging of the sample during the lithography process. On top of the Cu a 50 nm thick PMMA 950k layer is spun (Figure 5.3(c)). The antenna geometry is then exposed by EBL (Figure 5.3(d)) followed by the evaporation of 20 nm of gold (Au) by EBPVD (Figure 5.3(e)). Antennas sitting on a Cu film are then achieved by lift-off of the resist in acetone (Figure 5.3(f)). Optionally a 50 nm thick PMMA 950k layer can be spun on top of the antennas (Figure 5.3(g)). This optional layer, after an etching step that will be discussed later, will form pillars under the antennas.

### 5.2.1 Pattern transfer

Once the antennas are patterned by EBL on a glass-Cu substrate as explained in the previous section, the antennas are ready to be transferred onto PDMS.
5.2. FABRICATION METHODS

A microscopy glass slide having a size of 76 × 26 mm² with a thickness of 1.5 mm is used as a base (Figure 5.4(a)). This glass slide has the same dimensions as the substrate used during EBL. Two spacers of the desired PDMS thickness are glued on each side of the base glass slide. In our case an other glass slide of 1.5 mm was sawed and used as spacer (Figure 5.4(b)). After mixing and defoaming the PDMS as described in section 3.1.2, the rubber is poured onto the base glass (Figure 5.4(c)). After the PDMS has spread the whole area (Figure 5.4(d)), the sample is pushed towards the PDMS (figure 5.4(e)&(f)). Pushing of the sample towards the PDMS should squeeze out the excess PDMS. After a curing time of at least 48 hours at room temperature, the sample is dipped into a nitric acid solution in order to etch away all the Cu. This step separates the antennas which are embedded into the PMMA from the top substrate (Figure 5.4(h)). An isotropic etching step in oxygen is performed in order to have free standing antennas and no more embedded ones into the PMMA (Figure 5.4(i)). In the following sections the details of the fabrication steps are discussed.
**Figure 5.4:** (a) A microscope glass slide is used as a base. (b) Two pieces of glass of the same thickness are glued onto the slides and play the role of spacer in order to get a homogeneous PDMS thickness. (c) After defoaming PDMS is poured onto the glass slide. (d) PDMS fills the entire slide up to the spacer. (e) The structures fabricated on the Cu/Glass slide is deposited on top of the spacers. (f) Top slide is pushed towards the bottom slide in order to squeeze out the excess PDMS. (g) Everything is put in a HNO$_3$ 1:10 H$_2$O mixture in order to etch the Cu away. (h) This leaves the structures completely embedded into PMMA. (i) After a plasma etching step, the structures are now sitting on top of the PDMS.

### 5.2.2 Copper lift-off

In order to etch away the Cu, the whole sample is dipped into a nitric acid solution (HNO$_3$ 1:10 H$_2$O). Before this step, the sample should be cleaned and all excess of PDMS on the edges should be removed in order to have a direct contact between the acid and the Cu.

Unfortunately as the Cu is only 50nm thick, the acid solution can flow only with difficulty between the base slide and the sample. We experienced a variable lift-off time between three days and one and a half weeks. A higher temperature can favor the etching process, but was not risked, as at the same time, PDMS would expand and alter the structures of interest. We also tried to double the Cu thickness, but this resulted in a negligible difference in the etching duration. As a thinner layer of Cu tends to be flatter, we kept the original 50nm thickness as the best choice.

Alternatively we tried a 90nm thick chromium (Cr) layer instead of Cu. Cr was etched in a mixture of ceric ammonium nitrate [ (NH$_4$)$_2$-Ce(IV)-(NO$_3$)$_4$ ] and acetic acid (CH$_3$COOH). After one week only a very small amount of Cr present at the border of the sample was etched. This alternative was abandoned and only the Cu layer was retained as a good solution.
5.2. PDMS etching

For the case of samples without a sacrificial layer of PMMA spun on top of the antenna before the transfer onto PDMS, the PDMS has to be etched in order to release the embedded antennas.

We etched the samples in a reactive ion etching (RIE) using an Oxford Instruments PlasmaLab 80 system. We used 80 sccm of SF$_6$ and 20 sccm of O$_2$ with a power of 50 W. After a 20 s etching step, the sample was investigated with an atomic force microscope (AFM). As shown in Figure 5.5, the antenna thickness coming out of the PDMS was about 16 nm. As the antennas should be 20 nm thick a second etching step of 20 s was performed. Again an AFM

![AFM measurement of 20 nm thick bowtie antennas transferred onto PDMS and etched by RIE (80 sccm SF$_6$ and 20 sccm O$_2$) for 20 s with a power of 50 W.](image)

(a) Topography acquired by AFM. The text DOSE comes from a label written by EBL. Two bowtie antennas are visible at a x-position of 3 µm.

(b) Topography profile performed on the letter “O” of the label (see figure (a)).

(c) Topography profile performed on the long axis of a bowtie antenna (see figure (a)).

Figure 5.5: AFM measurement of 20 nm thick bowtie antennas transferred onto PDMS and etched by RIE (80 sccm SF$_6$ and 20 sccm O$_2$) for 20 s with a power of 50 W.
profile was taken after this second step and a thickness of 25.1 nm was measured on the letter “O” of one of the labels (see Figure 5.5(a)) and 21.9 nm was measured on the same bowtie antenna as shown in profile 2 in Figure 5.5. We see an increase of 10 nm on the label, but only of 4 nm on the bowtie antenna compared to the last step. AFM is very difficult to be performed on a flexible substrate as a high material contrast exists between PDMS and gold. This implies that the measurement depends drastically on the tip–sample distance. We performed measurements with a higher zoom and a lower tip–sample distance leading to a thickness which was about half the one measured with a smaller zoom (i.e.: 10.7 nm versus 21.9 nm). We are convinced that a smaller tip–sample distance with a slower scan gives more realistic measurements. For this reason we performed a third etching step of 20 s. The bowtie thickness was again measured by AFM and was found to be 21 nm with a high zoom and a small tip–sample distance. A total etching time of 60 s was thus considered as optimal in order to have free standing antennas with a thickness of 20 nm.

Further optimisation of the PDMS etching was not performed, because later PMMA was used as a material for pillar formation.

5.2.4 PMMA etching

A layer of PMMA can be spun onto the antenna before the PDMS is poured (see Figure 5.3(g)), resulting in antennas embedded in PMMA after the Cu lift-off. An isotropic etching of PMMA results in pillar formation under the antennas (see Figure 5.1(c)).

PMMA is an organic material and can be easily etched by oxygen plasma. We performed this etching step in an oxygen plasma asher (TECHNICS PLASMA TEPLA 100 ASHER system using a 2.45 GHz microwave power) with a pressure of 0.7 Torr and a power of 200 W.

Etching calibration was performed on spun PMMA onto glass substrates. The samples were scratched with tweezers with rounded tips and the thickness of the PMMA was measured by a profilometer (DEKTAK SURFACE STEP PROFILER) across the scratches made before and after each etching step. First of all an etching step of 30 s was performed with a power of 200 W and a pressure of 0.7 Torr. Then a second step of 120 s was performed. The results are shown in Figure 5.6 where each color corresponds to a different test sample. Due to measurement uncertainties of the profilometer some of the thicknesses were measured several times on several scratches and are displayed as a boxplot. The etching rate deduced from the obtained thickness and was found to be 0.25 nm · s⁻¹ for PMMA at this power.
5.2. Fabrication Methods

Figure 5.6: Thickness measurement of a PMMA layer after successive oxygen plasma ashing steps with a power of 200 W and a pressure of 0.7 Torr. Each color corresponds to the measurement performed on a different sample. The black sample thicknesses is displayed with a fixed offset of 50 nm in order to avoid confusion with the blue one as their original thickness were identical. The fitted etch rate for each sample is visible in the subset. The average etch rate was found to be $0.25 \, \text{nm} \cdot \text{s}^{-1}$.

The transferred antennas onto PDMS are sitting on a 50 nm thick PMMA layer and thus require an etching time of 200 s. The antennas play the role of a shadow mask protecting the PMMA below it. This creates small pillars under each antenna.

5.2.5 Strain measurement

Strain was induced in the PDMS film by clamping the sample on two edges and stretching it by a home made device. This stretching device is made out of two screws having a fine thread which pull apart the two opposite edges of the PDMS sample. The presence of two screws allows optical measurements to be performed in transmission. A schematic of this stretcher is shown in Figure 5.7.

Turning the screws induces a global strain in the PDMS, but due to film inhomogeneities and relaxation, the local strain in the middle of the sample might differ from the global strain. In order to determine the local strain, we inscribed a ruler close to the structures of interests by EBL. A microscope image of the ruler was performed (see Figure 5.8(a)) at each stretching step.

The spacing between the ruler lines was then measured by taking a profile (see Figure 5.8(b))
**Figure 5.7:** Schematic of the stretching device. The flexible substrate is clamped on two metallic bars which are separated by a fixed distance which can be controlled by two long screws. Two metallic rods are present at the bottom of the holder to guide the two plates. The configuration of the stretcher provides a direct optical access to the sample from both sides allowing measurements to be performed in transmission.

**Figure 5.8:** (a) Microscope image (false color) of the ruler which was inscribed by EBL in the middle of the sample. (b) Intensity profile along the line displayed in Figure (a) The red lines correspond to the peak maximum positions. (c) The peak positions are fitted in order to obtain the average ruler spacing in pixels. (d) The local strain compared to the number of turn applied to the stretcher (global strain) is shown. The PDMS is stretched by applying different number of turns of the stretching screw which are displayed on the x-axis. The y-axis shows the corresponding strain measured on the ruler.
where the average tick separation was fitted (see Figure 5.8(c)). The local strain can now be calculated as the ratio between the average tick spacing under a given strain compared to the average spacing when no global strain is applied. Figure 5.8(d) shows the local strain in function of the number of turns applied to the stretching screw.

### 5.3 Optical characterization and simulations

Bowtie antennas of various sizes and shapes were fabricated. Transmission electron microscopy (TEM) images of such bowtie antennas fabricated on a 30nm thick silicone nitride membrane are shown in Figure 5.9. Those images display the polycrystalline grain structure of the evaporated gold forming the antennas. As it can be seen antennas having different sizes and geometries could be achieved. We fabricated similar bowtie antennas on PDMS as described previously in this chapter. In the following we compared the tunability of the optical response of bowtie antennas fabricated on PDMS with and without the presence of a PMMA pillar under them. Later we simulated the effect of various geometrical variations on bowtie antennas.

![TEM images of bowtie antennas produced by EBL with an energy of 30 keV and lift-off of 20 nm of gold. The TEM image display very well the polycrystalline grain structure of the gold which was deposited by electron beam physical vapor deposition.](image)

**Figure 5.9:** TEM images of bowtie antennas produced by EBL with an energy of 30 keV and lift-off of 20 nm of gold. The TEM image display very well the polycrystalline grain structure of the gold which was deposited by electron beam physical vapor deposition.

#### 5.3.1 Tunability of antenna on PDMS

We fabricated bowtie antennas on PDMS with the pattern transfer method as described in section 5.2.1 without PMMA deposited on top of the structures before the PDMS was poured.
This resulted in gold antennas lying directly on the PDMS surface. Scanning electron microscope (SEM) images of the obtained antennas after transfer are shown in Figure 5.10. The antenna shown on the left has a total span length of $406 \pm 4$ nm with a gap of $10 \pm 4$ nm. The one on the right has a length of $394 \pm 4$ nm and a gap size smaller than $6$ nm. Due to charging to obtain the exact dimensions of the antennas with a higher precision is difficult. The charging effect is visible on the SEM images as dark regions in the vicinity of each antenna. For this reason it is also not excluded that the antenna shown in Figure 5.10(b) is gapless.

![Figure 5.10: SEM images of bowtie antennas transferred onto PDMS. The left and right antenna have a total length of $406 \pm 4$ and $394 \pm 4$ nm respectively. The gap size is measured to be $10 \pm 4$ for the antenna shown in (a). The antenna shown in (b) has a gap size smaller than $6$ nm. Due to the high charging effect caused by the non-conductive PDMS substrate the gap size cannot be resolved with a higher precision.](image)

The scattering spectra of the antenna shown in Figure 5.10(a) and measured under different strain conditions is displayed in Figure 5.11. Each curve represents the spectrum obtained with a different strain applied to the PDMS. The intensity is displayed in arbitrary units and was normalized to zero at a wavelength of $550$ nm and to one at the maximum intensity of each spectrum. The curves are shifted vertically by an intensity of $0.05$ for each strain for clarity. The bottom curve was recorded with the lowest strain and the top one with the highest. The exact strain values are shown in the top-left inset. The antenna presents two resonance peaks. The strongest one is the dipolar mode as it has the largest wavelength and is the strongest (highlighted in red in the figure). The one with higher energy, and thus lower resonance wavelength, is probably the quadrupole mode and is highlighted in blue.

For the case of the dipole mode, the electric field is concentrated into the gap and thus the resonance of the mode depends strongly on the gap size of the antenna. In our case we see
5.3. OPTICAL CHARACTERIZATION AND SIMULATIONS

Figure 5.11: (a) Scattering spectra of bowtie antenna on PDMS under different substrate strain. Each curve is shifted by a fixed amount in the y-direction for clarity (lowest curve corresponds to the lowest strain). (b) Resonance wavelength of the dipole peak highlighted in red in figure (a). (c) Resonance wavelength of the quadrupole peak highlighted in blue in figure (a).

that the resonance shift of the dipole mode per strain percent reaches $-0.81 \text{ nm/%}$ (see Figure 5.11(b)). Under strain, the gap size of the antenna becomes larger leading to a blue shift as expected from theory and verified in simulations (see section 5.3.4). A strain of 10% leads to a resonance shift of only 8 nm. Measurements performed on similar antennas have reported similar values, but this value is small compared to the measurement uncertainty of the resonance wavelength.

The quadrupole mode is less sensitive to gap size variations, but more generally to the geometry of the antenna and thus its total length (see simulation results later). Shifts of the resonance of this mode will be dominated by the antenna total length and presence of defects. In our case the trend of the resonance behavior as a function of the strain is not very clear for the quadrupole peak. We observe a general trend towards a slight redshift (see Fig-
Measurements performed on similar antennas were also obtained with no specific trend for the quadrupole peak sensitivity. Values between $-0.2 \, \text{nm/}%$ and $0.1 \, \text{nm/}%$ were measured. We believe that those differences in behaviors came from strain relaxation and crack formation during the stretching. This can also explain jumps in the resonance wavelength during the stretching as seen in Figure 5.11(c) between 3% and 4% strain. Unfortunately AFM (see section 5.2.3) and SEM (see Figure 5.10) measurements don’t have sufficient resolution to resolve those cracks.

In order to increase the tunability of the antenna and avoid the potential formation of cracks, a method to create antennas on pillars was exploited (see Section 5.2) and the results obtained with these antennas are presented in the next section.

### 5.3.2 Tunability of antenna on pillars

The scattering spectra of bowtie antennas sitting on PMMA pillars were measured under different strain conditions. The results for bowtie antennas having a total size of $300 \pm 10 \, \text{nm}$ are shown in Figure 5.12. The left column displays the scattering spectrum measurement for different antennas having the same fabrication parameters. Each curve was recorded under a different strain between 0 and 6.8%. The resonance wavelength was fitted by Lorentzians from the measurements and expressed as a function of the strain (see right column). The first antenna shows a resonance shift of $-3.04 \, \text{nm per strain percent}$ which is a large improvement compared to the $-0.52 \, \text{nm/}%$ measured for antennas without pillars (see previous section).

Optical characterization and determination of the exact geometry of the antenna deposited on PDMS/PMMA is a very complex task. Investigations of the antennas under SEM lead to a drastic change of the properties of the antennas. The effects are already visible optically as it can be seen in Figure 5.13(a). The figure shows a microscope image of an array of bowtie antennas. Antennas which were investigated by SEM in an earlier stage are scattering the light in a very different way compared to other antennas (see the bright spots). Here two effects are important. First, electron bombardment of the PMMA weaken and breaks some molecular bindings. Investigations of PMMA by SEM will thus change the material properties itself. Second, the electron beam of the SEM will react with the residual particles present in the chamber, mainly organic molecules, and will thus deposit a thin layer of material, mainly carbon, onto the sample. This carbon contamination will load the gap of the antenna leading to a drastic change on the optical properties. For those reasons the inspection of the sample
Figure 5.12: Left) Spectra measurement of bowtie antennas having a total length of 300 nm under different stretching condition. Right) Resonance wavelengths of the antenna as a function of strain. Each row presents the result of a different bowtie antenna, which were all fabricated with the exact same parameters.
Figure 5.13: Images of bowtie antennas array(s) taken by an optical microscope with a dark field illumination. (a) Abnormal scattering coming from antennas which were previously investigated by SEM. (b) Four arrays of 10x10 antennas each on PDMS without strain. (c) Image taken with a strain of 7% applied to the PDMS. Cracks and other artifacts become visible on top of the substrate with high strain creating a lot of scattering. The three antenna arrays shown on the top of the image are nearly invisible by eye. The three arrays shown on the bottom of the array were previously imaged by SEM leading to a reduction in scattering.

by SEM should be avoided before any optical characterization. Alternatively characterization of the antennas geometry by AFM was also tried (see section 5.2.3) but gives a very bad contrast due to the softness of the substrate. This implies that optical characterization has to be performed without having information on their exact geometry.

Antennas on unstrained PDMS are well visible and scatter enough light to be detectable as shown by the optical microscope image in Figure 5.13(b). At higher strain the substrate becomes more and more opaque and scatters more and more light. An image of a sample strained by 6% taken with an optical microscope with dark field illumination is shown in Figure 5.13(c). The top row shows that the substrate is scattering enough light that the antennas are no more visible by eye. Antennas can be still detected by our spectrometer, but the scattering coming from the substrate usually cannot be subtracted easily. This effect is visible in Figure 5.12(left column) where the infrared part of the spectrum of sample strained by 6.8% shows a much higher signal than of lower strain. Scattering from the substrate probably explains why the resonance wavelength of the strained antenna is shifted towards the infrared (see Figure 5.12(c)&(d)). The global trend for this antenna was found to be only $-1.5 \text{nm/\%}$, but discarding the measurement with the highest strain due to the background scattering problem results in a tunability of $-4.2 \text{nm/\%}$. Most of the measurements for similar antennas
have shown a tunability between $-2.3\,\text{nm}/\%$ and $-4.2\,\text{nm}/\%$.

Some antennas showed a strange behavior of their resonance under stress like the ones presented in Figure 5.12(e) and Figure 5.12(f). The global tunability (discarding the last point due to scattering issues) leads to a very low tunability of $-0.53\,\text{nm}/\%$ which is comparable to results for antennas without pillars (see previous section). One possible explanation for this low tunability is that the pillars were not etched correctly and that only a single pillar forms leading to a similar tuning capability as antennas without pillars.

The characterization of the antenna geometry by SEM was found to be problematic due to the fact that PDMS and PMMA are non-conductive. Charging and drifts occur during the measurements reducing the image quality and thus only an approximative geometry can be measured from those images. The deposition of a 5 nm thick Cu layer before performing SEM can reduce the charging problem, but at the same time also decreases the imaging resolution due to electron scattering inside the Cu layer. An approximative gap size of $32 \pm 7\,\text{nm}$ was measured on a SEM image for the antennas presented in Figure 5.12. This gap size was confirmed by our simulation as will be shown in section 5.3.8.

5.3.3 Simulations of the near field at the resonance modes of antennas

Simulations of bowtie antennas were run similarly to the dipole antennas (see Chapter 4). Bowtie antennas have several resonance peaks as it will be demonstrated in the next section. In order to understand the nature of each resonance, the norm of the electric field can be simulated and analyzed. Simulation results of the norm of the electric field at the sample–air interface for a bowtie antenna having a total span length of 300 nm and a gap size of 10 nm are shown in Figure 5.14. The left column displays the near field for the wavelength at the highest resonance mode of the antenna (i.e.: $\lambda = 960\,\text{nm}$) which corresponds to the dipole mode. The right column displays the near field for the second resonance mode of the antenna ($\lambda = 870\,\text{nm}$). This second mode is less strong in intensity and presents a lower resonance wavelength. We assume that this mode corresponds to higher order mode. Each row presents the same result for an antenna excited with a different polarization angle. $0^\circ$ corresponds to a linear polarization along the long axis of the antenna and $90^\circ$ to a polarization along the short axis of the antenna. The difference between the two modes is best seen with a $45^\circ$ polarization, where the dipole mode has a strong and dominant electric field in the antenna gap. The higher order mode displays an equivalent field strength at all the antenna corners as well as in the gap.
In the rest of this chapter we will concentrate on simulations of the resonance of the dipole mode exclusively as it displays the highest intensity and is more sensitive to the gap size of the antenna.

Figure 5.14: Simulated norm of the electric field of bowtie antenna having a total length of 300 nm and a gap of 10 nm sitting on a 20 nm PMMA layer on top of a PDMS substrate. The displayed data are a cross section taken at $z = 0$ (i.e.: at the intersection between the antenna and the PMMA layer). The left column was simulated with an incident illumination having a wavelength of 960 nm, while the right one with 870 nm which correspond to the dipolar and a higher order resonance frequencies of this geometry. Results for different polarization angle of the incident illumination where simulated.
5.3.4 Simulations of bowtie antennas with various gap sizes

Bowtie antennas are formed by two dimers separated by a gap. The gap size plays a key role in the resonance property of the antenna as it was already demonstrated for dipole antennas in Chapter 4.

The simulation results for bowtie antennas having a total length of 300 nm and a thickness of 20 nm and various gap sizes are presented in Figure 5.15. Small gap sizes present a resonance in the infrared while larger gaps show a resonance with a shorter wavelength. Simulations were fitted with Lorentzians in order to determine the resonance wavelength of each antenna. The higher order mode present at around 800 nm is well visible for antennas with a large gap. The size of our computational domain is limited by the computer memory. This implies that electromagnetic waves with a higher wavelength will be less accurately simulated and some artificial reflections and scattering might occur. This effect can be visible by the difference between the Lorentzian fitting and the results of the simulations for small gap sizes (see black and red curve on the right in Figure 5.15).

The resonance behavior as a function of the gap size is summarized in Figure 5.16 for antennas of various sizes. Antennas having a total length of 300 nm on PMMA and 400 nm on PDMS are shown by blue circles and magenta squares respectively. For comparison, antennas with a fixed arm length of 150 nm are shown by red triangles. The resonance has an exponential behavior as it can be seen by the blue, red and magenta curves and is similar to the one for dipole antennas (see Chapter 4). The resonance shift per gap size unit increases for small gaps, however the tuning capability is proportional to the gap size of the antenna. The green curve shows the tunability of an antenna having a total length of 400 nm on PDMS. The tunability is defined here as the resonance wavelength shift for a gap size increase of 10% of its value at rest. The best tunability is reached for antennas having a gap size of about 11 nm (see minimum of the green solid curve) with a resonance shift of about $-0.6 \text{ nm/\%}$.

Our measurements performed without pillars had a similar gap size (10 nm) with a tunability of $-0.81 \text{ nm/\%}$ which is in quite good agreement with the simulations. Simulations of the tunability of antennas having a total length of 300 nm are shown for comparison (green dashed curve). In this case the substrate was PDMS coated with a 50 nm PMMA layer. Simulations show a similar tunability for antennas with a gap size of 30 nm compared to antennas with a total length of 400 nm and a gap size of 10 nm. Due to the presence of PMMA pillars, we measured an enhancement of the tunability of about a factor 5 which is a good improvement.

For coherence with Chapter 4 we kept the total length of the antenna constant and varied only
the gap size. Simulations of antennas with a fixed arm length of 150 nm instead of a constant span length of 300 nm were also performed for comparison (red triangles). We simulated a resonance wavelength of 873 nm for a single triangle (i.e.: antenna composed of only one arm) having a total size of 150 nm, which is similar to an antenna with an infinit gap and matches well with the offset value of the fitted curve (red dashed curve). The resonance wavelength of a gapless antenna was simulated and found to be 1244 nm. This value was used during the fitting for the amplitude term in the exponential function. The amplitude term is equal to 1244 minus the offset term.

### 5.3.5 Simulation study of antenna arm length asymmetry

The fabrication of bowtie antennas is never perfect and the length of each antenna arm might differ slightly. We simulated bowtie antennas having a fixed span length of 300 nm, a gap size of 10 nm and a thickness of 20 nm but varying arm length asymmetries. Results are shown in

![Simulation of bowtie antennas having a total length of 300 nm, a thickness of 20 nm on a 20 nm thin PMMA layer on a PMDS substrate. The simulations are performed for various gap sizes. Antennas with small gaps lead to a resonance in the near infrared, while antennas with larger gaps have a resonance at a shorter wavelength.](image)

**Figure 5.15:** Simulation of bowtie antennas having a total length of 300 nm, a thickness of 20 nm on a 20 nm thin PMMA layer on a PMDS substrate. The simulations are performed for various gap sizes. Antennas with small gaps lead to a resonance in the near infrared, while antennas with larger gaps have a resonance at a shorter wavelength.
Figure 5.17. In the case of perfect symmetry both arm lengths are equal to $\frac{300 - 10}{2} = 145$ nm. The behavior of the resonance wavelength as a function of the antenna asymmetry is shown in Figure 5.17(b). We see that small variations of the arm length asymmetry has a small impact on the resonance shift. Typical arm length difference measured on our fabricated antennas is in the range of 10 nm. According to our simulations this results only in a shift of 1 nm of the resonance wavelength, which implies that small asymmetries in the arm length can be neglected. Symmetrical antennas can be simulated on a computational domain which can be reduced to one quarter of the total volume (see chapter 3). Reduction of the computational volume, implies that a finer meshing can be used and thus a higher accuracy is reached.

**Figure 5.16:** Simulation of the resonance wavelength in function of the gap size of bowtie antennas having a thickness of 20 nm. Simulations on a 20 nm thin PMMA layer on a PDMS substrate for antennas having a total length of 300 nm (blue circles) or a fixed arm length of 150 nm (red triangles). Antennas on PDMS (wo/ PMMA) having a total length of 400 nm was also simulated (magenta squares). The tunability of the antenna is defined as the resonance shift for a gap size increase of 10% (see green curves with the corresponding y-axis on the right).
(a) Simulations for the scattering intensity of the antennas. The curves are a Lorentzian fitting from the simulation results. The perfect symmetry is for antennas having an arm length of 145 nm which correspond to the minimum of the second order fit.

Figure 5.17: Simulations for the scattering intensity of bowtie antennas having a total size of 300 nm and a gap size of 10 nm. Asymmetries between the left and right arm length are shown in the inset. The highest simulated asymmetry (left arm length=90nm) shows a resonance in the IR, while more symmetric antennas have a resonance more towards the blue.

5.3.6 Simulation study on antenna span length

Antennas with a fixed gap size of 5 nm were simulated for different lengths. Their resonance wavelength as a function of their total length is shown in Figure 5.18. The resonance wavelength change per length was found to be 1.51 (see fit shown in blue). This number is in good agreement with previous simulations [FM08]. Here we can provide a clear and consistent trend compared to the cited result. The trend of the resonance going into the infrared for longer antennas can be easily understood by the fact that plasmon forming standing waves at resonance scale with the antenna arm length. In section 2.2.1 we have demonstrated that the Mie-Gans theory agrees well with this linear behavior for gold in the visible. This linearity can be also seen in the wavelength-scaling relation (see section 2.6) where the effective wavelength (\(\lambda_{\text{eff}}\)) is proportional to the resonance wavelength (\(\lambda\)) for the case where \(\lambda > 550\) nm.

The scattering intensity of the antennas at resonance have been demonstrated to have a quadratic relation to the total antenna length. Optical measurements on antennas require a high scattering intensity and thus the antenna length should be as large as possible in order
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Figure 5.18: Simulations for the resonance wavelength (blue curve) and intensity (red curve) of bowtie antennas having a fixed gap size of 10 nm and for various lengths.

to reach the highest possible intensity. But the experimental detection limit of our spectrometer was 1200 nm. For this reason the fabrication and measurements were focused on bowtie antennas having a total length of 300 nm.

5.3.7 Simulations using star-shaped bowtie antennas

Fabrication of small bowtie antennas with a low dose during the EBL can result in star-shaped antennas as discussed in Chapter 3. This fabrication strategy was used for antennas having a total length of 200 nm. Simulations of such antennas are shown in Figure 5.19. Star-shaped antennas with a gap size of 5 nm show a resonance at 944 nm while triangular ones with the same length and gap (see Figure 5.18) show a resonance with a shorter wavelength (860 nm). As antennas with a resonance wavelength further in the infrared are harder to measure due to the detection limit of the detector, this fabrication strategy was not further exploited and studied. Moreover star-shaped antennas were found experimentally to scatter much less light than regular bowtie antennas.

5.3.8 Simulations of antennas on pillars

The implementation of the substrate in the simulations of optical antennas is challenging. We were able to simulate multi-layered substrates as described in Chapter 3. We applied a
 technique using the theoretically derived values for the incident illumination propagating through the substrate and its additional PMMA layer. With this technique, the presence of surface roughness and other irregularities cannot be simulated easily. An other problem is that the exact geometry of the pillar cannot be resolved with our characterization techniques. For this reason the simulations presented in the above sections were all performed with a continuous and perfect layer of PMMA (i.e., antennas lying directly on the PMMA layer).

Simulations performed and discussed above show a resonance wavelength which lies more towards the infrared compared to the measured ones. As shown above, bowtie antennas having a total length of 300 nm and a gap size in the range between 5 nm and 50 nm have a resonance wavelength which lies between 900 nm and 1240 nm in our simulations compared to 750 nm to 850 nm for the measurements. In order to explain and understand this difference we simulated bowtie antennas having a total length of 300 nm and a gap size of 10 nm sitting on a PMMA pillar having the same geometry as the antenna. The arm length of the pillar

Figure 5.19: Simulation of the scattering spectrum for star shaped bowtie antennas having a total length of 200 nm, a width of 30 nm and a thickness of 20 nm. The circles are the simulated values, the lines correspond to a Lorentzian fit of the points. The center wavelength of the Lorentzian fit is displayed on the top of the figure. Values written in the middle correspond to the FWHM of the resonance.
was defined as the antenna arm length minus twice the pillar undercut (see Figure 5.20(a)). The results for the scattering spectrum for different pillar undercut sizes are shown in Figure 5.20(b). We notice, that even a pillar without undercut (black solid curve) results in a resonance wavelength of 900 nm compared to 958 nm for the case of a continuous PMMA film. This blue shift is even larger for larger undercuts (ie. smaller pillars).

![Figure 5.20](image)

**Figure 5.20:** Simulations for bowtie antennas sitting on a PMMA post having the same geometry as a bowtie antenna but with a length per arm reduced by twice the pillar undercut value. (a) Schematic of the geometry of the pillars and definition of the pillar undercut. (b) Simulations of the scattering spectra with different undercut values for bowtie antennas having a gap size of 10 nm (solid curve). Higher undercuts (ie. thinner pillars) lead to a resonance wavelength shifted towards the blue. The simulation for bowtie antenna with gap size of 30 nm on a pillar without undercut (dashed curve) is very similar to the measured values. (c) Resonance wavelength behavior in function of the pillar undercut size. The red curve shows an exponential fitting of the simulations.

We simulated bowtie antennas matching the fabricated ones as closely as possible (see Section 5.3.2). Simulations were performed for a total length of 300 nm, a gap size of 30 nm, a thickness of 20 nm sitting on a 30 nm thick PMMA pillar on a PDMS substrate. The result
is shown in Figure 5.20(b) (dashed curve) and displays a resonance at around 820 nm for the dipolar mode and at around 750 nm for the higher order mode. The measurements presented in Figure 5.12 (see section 5.3.2) show very similar resonance frequencies.

5.4 Conclusion

The fabrication of bowtie antennas on a flexible substrate, such as PDMS, was demonstrated to be possible by fabricating such structures on a hard substrate followed by a transfer onto PDMS. The chosen technique was demonstrated to be applicable with a number of different technologies but was shown to be time consuming due to the transfer step from the hard substrate onto PDMS.

The high flexibility of the substrate and its sensitivity to temperature and humidity variations can create local changes of the initial design. Fabrication of different antennas with the exact same fabrication parameters can result in different geometries and gap sizes. This was confirmed by the measurements of different optical responses of bowtie antennas created with the same parameters. The procedure cannot be considered to be as reliable as the fabrication of antennas on a hard substrate.

The use of PMMA as material for the pillar layer was found to improve the antenna tunability. But this material presents two drawbacks. First, high stretching of the PDMS film creates cracks in the PMMA layer leading to a lot of scattering which perturbs the optical measurement of the antennas. Second, most of the solvents, such as acetone, di- and trichloromethane and tetrahydrofuran (THF), dissolve PMMA. For this reason antennas on PMMA pillars cannot be used after fabrication for biosensing applications where molecules are generally diluted in solvents before being deposited on the antennas. We believe that the antennas on pillar fabrication technology can be adapted to other polymers in order to replace the PMMA. Polyimide might be a good alternative as it is stiff and resistant to solvents.

We have demonstrated a high increase of the tuning capability of optical antennas fabricated on pillars (up to $-4.2 \text{ nm}/\%$) compared to antennas fabricated directly on the PDMS surface ($-0.8 \text{ nm}/\%$). This represents an improvement of a factor five. PDMS can stand a strain of about 10% which can lead to a resonance wavelength shift of up to $-42 \text{ nm}$ which corresponds to 50% of the FWHM of the antenna resonance. The technology presented here can find its application in biosensing and Raman spectroscopy.
Chapter 6

Optical antennas for Raman signal enhancement of molecules

6.1 Introduction

The resonance wavelength of optical antennas is sensitive to the effective refractive index in the vicinity of an antenna. The presence of molecules in close proximity to the antenna changes the local refractive index and thus its resonance wavelength. This technique is quite efficient for binding event tracking [ZHSM10], but can be used only to count the number of binding events and cannot determine the types of molecules. If one is interested in the detection of specific type of molecules, the antenna can be coated with antibodies so that only a particular type of molecule can bind with the antenna [AHL+08]. If different types of molecules are to be detected, several antennas coated each with a different antibody are required.

Another technique consists in measuring the Raman signal coming from a molecule in order to determine its structure. Nanostructures can enhance this signal so that it is detectable even for a single molecule [KWK+97]. As metallic particles separated by small gaps have a very high local field enhancement [MLAS12], optical antennas become very interesting for the enhancement of Raman signals. They have already been successfully used for enhancing the signal for vibrational spectroscopy [AYA+09] as well as for Raman spectroscopy [ZFSM09].

In this chapter we complement the actual knowledge by performing an extensive study of the enhancement of the Raman signal by optical antennas and the tuning of this enhancement by varying the gap size of the antennas. This study will also include simulations of the Raman
enhancement factor for various antennas.

In the following we describe in detail the working principle of Raman scattering and how it can be used for molecular detection.

When photons are scattered from an atom or a molecule, most photons are elastically scattered, meaning that the scattered photon has the same energy as the incident one. This elastic scattering is more commonly known as Rayleigh scattering (see Figure 6.1).

Molecules are composed of several atoms linked together by covalent bonds which possess discrete energy levels. If a photon is absorbed by a molecule in a vibrational state \( \nu \), this molecule can re-emit a photon with a higher or lower energy by relaxing to a vibrational state with a higher or lower energy (\( \nu + 1 \) or \( \nu - 1 \)), respectively. This process is called Raman scattering.

![Figure 6.1: Energy levels of an atom or molecule and the possible electronic transitions due to photo absorption/emission. From the left to the right: IR absorption: A photon with low energy can be absorbed by the molecule to excite it to a higher vibrational level. Rayleigh scattering: A photon is absorbed and elastically re-emitted with the same energy. Raman: The difference in energy between the absorbed and re-emitted photon is the energy difference between two vibrational states. Fluorescence: The molecule is excited to a higher energy level which can be followed by non-radiative decays. The molecule relaxes to the ground state (E=0) via one of the vibrational states \( \nu \). Non-radiative decays can follow to bring the molecule back to its original state. Here emission can happen for various energies leading to a broad spectrum emission.](image-url)
(see Figure 6.1).

By looking at the energies at which Raman peaks occur, one can gain information about the molecular structure under investigation. This method is very suitable for label-free sensing as it does not require the presence of anti-bodies. Unfortunately the scattering cross section for Raman scattering is usually very small. First of all, this implies that the inelastic scattering wavelength has to be filtered out of the measurements in order to see the Raman peaks. Second, this means that a low concentration of molecules, and by extension single molecules, don't give a high enough Raman scattering signal to be detected.

Optical antennas have the ability to convert far field radiation into near field and concentrate it into its small gap volume. One can take advantage of an optical antenna in order to enhance the Raman signal emitted from a single molecule. This leads to a Raman enhancement factor \( g \) which can be approximated by Equation 6.1, where the left hand side represents the enhancement of the incident light having a wavelength \( \lambda_{\text{laser}} \). The right hand side of the equation describes the enhancement of the Raman signal which is emitted by the molecule at a wavelength \( \lambda_{\text{Raman}} \) [Sch11, ZFSM09].

\[
g = \frac{|E_{\text{loc}}(\lambda_{\text{laser}})|^2}{|E_{\text{inc}}(\lambda_{\text{laser}})|^2} \cdot \frac{|E_{\text{loc}}(\lambda_{\text{Raman}})|^2}{|E_{\text{inc}}(\lambda_{\text{Raman}})|^2}
\]  

(6.1)

In reality this equation is only an approximation as it ignores the effect coming from the polarization of the molecule with regard to the electric field.

In this chapter we investigated the Raman signal of dipole antennas with small gap sizes with and without the presence of molecules. All the antennas measured and discussed in this chapter are identical to the ones analyzed and discussed in Chapter 4.

6.2 Methods

This section is divided in two main parts. First, the description of the setup and the molecules used is presented. Then the method for computing the Raman enhancement factor from simulations is presented.
6.2.1 Raman setup

The Raman setup used was a single-stage confocal Raman spectrometer (Scientific LabRam HR) from the company HORIBA which has three excitation lasers with a respective wavelength of 532, 632.8 and 785 nm. As illustrated in Figure 6.2, the illumination consists of a laser followed by a beam shaper in order to remove speckles of the laser. The beam is then reflected on a semi-transparent mirror towards an objective which focuses the light on the sample. The scattered light is collected back by the objective and goes through an edge or a notch filter in order to remove the laser line. These filters are based on an interferometric technology using several thin films and can be slightly adjusted in order to tweak the edge position of the filter. The detected signal is analyzed by a spectrometer using a $300\text{mm}^{-1}$ grating and a nitrogen cooled detector.

![Diagram of Raman setup](image)

**Figure 6.2:** Raman setup used. The system uses an internal He-Ne red laser (632.8 nm) or an external laser (UV / green (532 nm) / IR (785 nm)). A beam shaper is present after the lasers in order to remove the speckles. The incident laser is then deflected by a semi-transparent mirror to a microscope objective which focuses the light on the sample. The scattered light is collected back by the objective. A notch or a band-pass filter suppress the reflection of the illumination laser (elastic scattering). The light is then sent to a spectrometer in order to resolve the wavelength of the inelastically scattered light.

6.2.2 Molecules

Two different molecules were used in order to test the enhancement capability of our antennas: chromophore and brilliant cresyl blue. They are described in the following sections.
6.2. METHODS

**Figure 6.3:** Chemical composition of the chromophore molecule used to test our antennas.

**Chromophore**

As depicted in Figure 6.3 the chromophore molecule used has two R-S-COCH$_3$ groups which hydrolyze to R-S-OH + H-COCH$_3$. The thiol group containing the sulfur atom reacts with gold and forms a strong bond with it.

A solution of 1 mM of the molecule in tetrahydrofuran (THF) was mixed in an agitator for several minutes and then poured on top of the sample covering the optical antennas. After two minutes, the sample was rinsed with THF in order to remove the leftover molecules and leave only the molecules that bound with gold.

The molecule has a span length of around 2 nm and fits perfectly into the gap of our antennas.

**Brilliant Cresyl Blue**

The second molecule used here is brilliant cresyl blue (BCB) (see Figure 6.4). This molecule has no chemical group which can bind with gold. For this reason it was spun onto the sample.

A solution of 1 mM of BCB in dichloromethane was spun for 60 s at 2 krpm onto the sample. As the sample is small, thin and brittle, a higher spinning speed was not tried in order to avoid potential damage and loss of the sample.
6.2.3 Raman enhancement

Optical antennas concentrate incident light in their gap region and induce a high field enhancement. In reality not only one molecule is to be found in the middle of the gap, but several tens to hundreds of thousands of molecules are expected to be excited by the laser beam in the case of spun molecules on the sample. Each of these molecules will scatter the Raman signal more or less efficiently according to the effective field enhancement at the location of the molecule. In order to estimate the effective Raman signal enhancement which is measured for the peak located at 657.1 nm (see Equation 6.1), the sum of the enhancement for each molecule over the area covered by the Gaussian illumination is to be considered. This means that our effective Raman enhancement $g$ will be an average of the Raman enhancements of all molecules:

$$g = \frac{1}{S} \sum_{j=1}^{N} \left[ \left| E(\lambda = 633 \text{ nm}, x_j, y_j, z_j) \right|^2 \cdot \left| E(\lambda = 657.1 \text{ nm}, x_j, y_j, z_j) \right|^2 \right]$$

(6.2)

where $j$ is the index of the molecule positioned at $(x_j, y_j, z_j)$, $N$ the number of molecules illuminated by the beam and $S$ a normalization factor so that $g = 1$ when no antenna is present:

$$S = \sum_{j=1}^{N} e^{-\frac{(x_j-x_0)^2+(y_j-y_0)^2}{\sigma^2}} |E_0|^4$$

(6.3)

where $\sigma$ corresponds to the beam radius of the Gaussian illumination, $(x_0, y_0)$ the beam center ($z$ is the propagation direction) and $|E_0|$ to the norm of the incident beam electric field in its center on the sample interface. As the molecules are present only at the sample surface ($z = 0$) or close to it ($z_j < 50 \text{ nm}$), the intensity of the Gaussian beam is considered to be constant.
6.3 Results & Discussion

In reality it is impossible to know the exact position of each molecule and a uniform distribution will be used to estimate an approximate value of the Raman enhancement. Equation 6.2 can now be simplified to:

\[ g = \frac{4}{|E_0|^4 \pi \sigma^2} \int_{R^2} dxdy \left| E(\lambda = 633 \text{ nm}, x, y, z = 0) \right|^2 \cdot \left| E(\lambda = 657.1 \text{ nm}, x, y, z = 0) \right|^2 \]

(6.4)

where we integrate over the substrate interface which is not covered by the antenna.

Our simulations are performed on a finite computational domain which had a radius \( R \). The electric field is assumed to have a norm \( |E_0| e^{-\frac{x^2+y^2}{\sigma^2}} \) outside this region and thus the factor \( g \) can be approximated as follows:

\[
g = \frac{4}{|E_0|^4 \pi \sigma^2} \left[ \int_{[R^2]} dxdy M(x,y) + 2\pi \cdot |E_0|^4 \int_R^\infty r e^{-\frac{4r^2}{\sigma^2}} dr \right] (6.5)
\]

\[
g = \frac{4}{|E_0|^4 \pi \sigma^2} \left[ 4 \int_0^{\frac{\pi}{2}} d\phi \int_0^R r M(r \cos \phi, r \sin \phi) dr \right] + e^{-\frac{4R^2}{\sigma^2}} (6.6)
\]

where the function \( M(x, y) \) was defined in Equation 6.4.

6.3 Results & Discussion

The setup was first calibrated by measuring the Raman signal from dipole antennas on a glass substrate with gap sizes in the range between 3.5 nm and 20 nm without the presence of molecules.

First the background was measured on the glass substrate (Figure 6.5).

The sample was illuminated with an incident wavelength of 633 nm. The decrease of the signal around zero is due to the notch filter which removes the laser line and thus the dominant Rayleigh scattering. On top of a broad background signal two small peaks are visible around 440 cm\(^{-1}\) and 920 cm\(^{-1}\) (see blue and green rectangle respectively in Figure 6.5). In the literature we found that the first peak corresponds to SiO\(_4\) in its tetrahedral form [WCH90]. Raman peaks are usually very narrow, but can get broader for amorphous materials such as glass [ZC93].

The glass substrate used was coated with a thin conductive titanium layer in order to avoid charging during fabrication. This thin layer oxidizes very quickly and forms an amorphous...
Figure 6.5: Raman signal measurement of the glass substrate coated with oxidized titanium. The excitation laser had a wavelength of 632.8 nm which was attenuated by a notch filter (gray). The small Raman signals are visible at 440 cm$^{-1}$ (blue) and 920 cm$^{-1}$ (green) which correspond to silicone oxide in its tetrahedral form and titanium oxide respectively.

TiO layer. It was demonstrated in [ABT84] that titanium oxide has a broad Raman peak at 920 cm$^{-1}$.

6.3.1 Raman measurements on dipole antennas

Raman measurements are performed on top of dipole antennas having a total span length of 130 nm. As those antennas have a resonance in the 650–750 nm range (see Chapter 4), a red laser (632.8 nm) was used in order to excite the antennas. The results are shown in Figure 6.6.

The black curves correspond to the raw Raman measurement. The red curves are the background measured on the substrate without the antenna (see previous section). The true signal coming from the antenna is shown by the blue curves and was calculated by subtracting the background signal from the raw signal. Those results can be easily fitted by a Lorentzian (see magenta curves). For comparison the scattering spectra acquired in transmission (see Chapter 4) are displayed in green and scaled to fit the plot region. They are in very good agreement with the Raman measurements.
6.3. RESULTS & DISCUSSION

Figure 6.6: Raman measurements with an excitation wavelength of 632.8 nm on a dipole antenna having a total length of 130 nm and a gap of 10 nm (left) and 12.3 nm (right figure). The blue curve corresponds to the real signal coming from the antenna which was calculated by subtracting the Raman signal measured on the antenna (black) by the one measured on the substrate (red). In comparison, measurements of the scattered intensity presented in Chapter 4 (green). A good agreement of the resonance wavelength with the blue signal is visible.

6.3.2 Measurements with chromophore molecules

After the sample was dipped in the chromophore solution, rinsed and dried, a stack of molecules accumulated in one corner of the sample. We used this location to measure the Raman signal of the molecules. The result is shown in Figure 6.7. The broad high peak is due to the fluorescence of the molecule and the three peaks highlighted at 677.8, 694.5 and 702.9 nm are due to Raman Stokes shifts.

Unfortunately no Raman peaks coming from the molecule were measured on top of the dipole antennas. The result is not shown here as it is identical to the ones displayed in Figure 6.6. This means that no Raman peak was visible in addition to the signal coming from the surface plasmon resonance of the antenna.

As antennas having a small gap size have a higher field enhancement (see chapter 4), we performed Raman measurements on antennas having a gap size between 3.5–5 nm. Antennas with such gaps have a resonance in the near-IR region (850–950 nm) and the red laser was thus not able to excite them. For this reason we used a diode laser having a wavelength of 785 nm as an illumination source. Measurements with this laser on the chromophore molecules are shown in Figure 6.8 (red curve). One of the advantages is that in this case no flu-
CHAPTER 6. OPTICAL ANTENNAS FOR RAMAN ENHANCEMENT

Figure 6.7: Raman scattering of the chromophore molecule (see Figure 6.3) using a He-Ne illumination laser (632.8 nm). The abrupt jump around 640 nm comes from the notch filter suppressing the laser line. Three main Raman peaks are visible. The displayed values are the center wavelength position of the Raman peaks.

Fluorescence occurs at this excitation wavelength. On the other hand the quantum efficiency of the camera is much lower and only a narrow region can be recorded. The limits of this region correspond to the edge of the notch filter which is around 790 nm (150 cm$^{-1}$) up to the detection limit of the camera which is around 1000 nm (2750 cm$^{-1}$). For this reason we were not able to resolve the strong Raman peaks of the methyl group which occurs at around 3000 cm$^{-1}$. The notch filter, used to cut out the illumination wavelength, uses an interferometric technique. This has the disadvantage to create interferences which are visible in the periodic oscillation of the signal (see Figure 6.8). Those interferences add to the noise signal and makes the detection of small Raman peaks very difficult.

Measurements performed on antennas require a very good alignment of the confocality of the system as excitation and collection of the signal have to come from the exact same spot: the antenna. After spending a lot of time optimizing the confocality and filter adjustment we measured a Raman signal on top of a dipole antenna having a gap size of 3.5 nm with an IR illumination (see Figure 6.8). The raw measurement is shown in black. The broad peak around 880 nm comes from the glass substrate (see blue curve). By comparing the raw
measurement with the signal measured on molecules (red curve) we cannot conclude the
presence of Raman peaks coming from the molecules. Nevertheless the localized surface
plasmon resonance of the antenna can be seen between 800 and 840 nm. This is in good
agreement with the spectroscopic measurements performed in transmission (see Chapter 4).

![Graph](image)

**Figure 6.8:** Raman signal taken on a dipole antenna having a gap size of 3.5 nm with an il-
 lumination laser of 785 nm (black curve). For comparison the measurement on chromophore
 molecules (powder) is also shown (red curve) as well as the measurement on the substrate (blue
curve).

The simulated Raman enhancement in the gap of a dipole antenna having a gap size of 3.5 nm
(see Equation 6.1) with an illumination of 785 nm for the Raman peak located at 881.3 nm
was found to be about $4.5 \cdot 10^6$. This enhancement is considered to be high enough for the
detection of a single molecule [GS09]. The absence of Raman peaks in the measurements (see
Figure 6.8) most probably implies that no molecules bounded to the antenna. In Chapter 4
we already had the suspicion of glass redeposition on top of the antenna during the milling
process. Glass coating of the antenna would prevent chromophore molecules from binding
with the antenna as these molecules only bind with gold. We can conclude from this that
redeposition of material during the fabrication process most probably coated the antenna
with at least one monolayer.

### 6.3.3 Measurements with brilliant cresyl blue molecules

Here we present an alternative to chromophore using brilliant cresly blue (BCB) molecules. A Raman measurement of the BCB molecule from its powder form is shown in Figure 6.9(a). The result displays several Raman peaks at 657.1, 683.1, 689.2, 695.8 and 706.7 nm on top of a large and broad fluorescence peak. Raman measurements performed on BCB spun on the glass substrate with an illumination of 632.8 nm with a power of 1.7 mW are shown in Figure 6.9(b). The lower density of molecules and the higher laser power photo-bleached the molecules suppressing the strong fluorescence. This allows us to resolve clearly the first Raman peak located at 657.1 nm (≈ 570 cm⁻¹). The four other Raman peaks measured from the powder (see Figure 6.9(a)) are highlighted in the figure. The peaks are also visible, but have a low signal-to-noise ratio.

![Figure 6.9: Raman spectra measurement of BCB. The illumination wavelength was 632.8 nm. Several Raman peaks are visible with their wavelengths highlighted. (a) Measurement on BCB powder with an illumination power of 1.7 µW. The broad background peak corresponds to the fluorescence of the molecules. (b) Raman spectrum of BCB molecules spun on a glass substrate. The rapid drop around 640 nm corresponds to the edge of the notch filter. The small peak around 633 nm comes from the laser.](image)

We measured Raman spectra of BCB molecules on top of several dipole antennas. The result on an antenna having a gap size of 17 nm is shown in Figure 6.10 (black curve). The red curve
displays the result for measurements performed on the substrate without the presence of an antenna. A Raman enhancement factor of 3.95 was achieved on this specific antenna. This factor was calculated by the ratio of the Raman peak intensities on the antenna compared to the background.

Figure 6.10: Raman measurement on a sample coated with BCB molecules. The red signal is the background measured on the glass substrate. The black curve is the measurement performed on a dipole antenna having a gap size of 17 nm. The blue curve corresponds to the measurement with the background subtracted. In magenta a Gaussian curve was fitted and corresponds to the resonance of the antenna.

Equation 6.5 was used with our simulations in order to determine a Raman enhancement factor. This one was found to be 9.01 for a dipole antenna having a gap size of 17 nm with an homogeneous coating of the substrate with molecules illuminated with a Gaussian beam of 700 nm of radius. The order of magnitude of this value is in good agreement with our measurement. The approximation used for the Raman enhancement supposes a uniform distribution over the whole substrate and that the Gaussian illumination is perfectly centered on the gap size of the antenna.
One important point is that antennas can present hot spots where the local field enhancement can be very high. From our simulations we have recorded a local field enhancement up to 120 in the hot spot of an antenna having a gap size of 5 nm. With such a high intensity, molecules located at those hot spots start to deteriorate. Those deteriorations can result in a decrease of the Raman signal coming from the molecule over time. A slow time dependency of the Raman signal was observed and a decrease of the Raman peak intensity was noticeable. For this reason the measurements were performed by integrating the signal over only 1 s and the illumination source was turned on at the same time as the measurement. This has two important disadvantages. First, each antenna can be measured only once. Second, a good focusing on the antenna cannot be performed and the implications of a slight defocus has to be estimated. In our case the focusing uncertainty was about 500 nm. This means that the distance separating the center of the illumination beam with the center of the antenna \(d\) can go up to 500 nm (see Figure 6.11(a)). The simulations of the Raman enhancement for different \(d\) are shown in Figure 6.11(b). We notice a decrease of the enhancement for larger \(d\). For different gap sizes and beam radii we notice an exponential decay of the enhancement factor. For an illumination having a beam radius of 500 nm, a defocus of 500 nm results in a decrease of about a factor \(e^4 \approx 54.\)

The Raman enhancement factors for several dipole antennas are shown in Figure 6.12. The measurements are represented by squares. Simulations of the Raman enhancement with a Gaussian beam illumination focused in the center of the antenna are shown by circles. The simulations of the Raman enhancement with a Gaussian beam focused with an offset of 500 nm with respect to the antenna center are shown by triangles. The illumination radius was estimated to be between 500 nm and 700 nm. The simulation results for both are displayed in red and blue, respectively. Our measurements lie between the simulation result for a perfect focus and a defocus of 500 nm. The equation presented in Figure 6.11(b) can be used to determine the defocus distance required in the simulation to achieve a similar Raman enhancement as the measurements. We found a defocus distance of 275–445 nm for a beam radius \(\sigma\) of 500 nm and a value of 215–540 nm for a beam radius of 700 nm. Those values are in good agreement with our estimation of 500 nm for a defocus distance.

The measured enhancement factors are quite small. This is due to the fact that molecules were present homogeneously everywhere and that a high signal is already measurable without the presence of an antenna. For the case of molecules present only on the antenna as it would be the case with chromophore molecules, a much higher enhancement is to be expected. In the case of a uniform coating on the antenna with molecules (but none on the
6.3. RESULTS & DISCUSSION

![Diagram](image)

**Figure 6.11: Effect of the focus position of the illumination beam on the Raman enhancement factor.** *(a)* Schematic of a slight defocus of a distance \( d \) between the antenna and the beam center. *(b)* Simulations of the Raman enhancement factor in function of the defocus distance \( d \) for a dipole antenna having two different gap sizes and different beam focuses. Note that the y-axis is displayed in log-scale.

Substrate), our simulations estimated a Raman enhancement in the range of \( 10^3 \). Antennas with smaller gap sizes lead to higher field enhancements at resonance. We have estimated by simulations that this Raman enhancement can reach \( 4.5 \cdot 10^6 \) for a single molecule present in the gap of a 3.5 nm dipole antenna illuminated with a wavelength of 785 nm.

Antennas can lead to a high increase of the Raman enhancement, but the resonance of the antenna has to match well with the illumination laser as well as with the wavelength of the Raman emissions. As the Raman setup used had only a limited number of illumination sources which have a fixed wavelength, a high Raman enhancement can be achieved by adjusting the resonance of the antenna by tuning its gap size. For this reason we believe that plasmonic antennas with tunable gap sizes are of great interest for Raman measurements of molecules. Unfortunately the tunable antennas that were fabricated and discussed in Chapter 5 could not have been tested here due to the incompatibility of the PMMA with the solvents required for the deposition the molecules.
Figure 6.12: Raman enhancement of the 657.1 nm peak with an illumination of 633 nm measured on dipole antennas having different gap sizes. The figure compares the results for the measurements (black square) with the simulations with an incident beam radius of 500 nm and 700 nm (red and blue respectively). The circles and solid line display the simulation result for a perfect focus alignment between the illumination beam and the center of the antenna. The triangles and dashed line show the simulation results for a focus offset of 500 nm between the illumination beam and the center of the antenna. The results for several defocus are shown in dotted lines (with defocus value written on top of each line).

6.4 Conclusion

We have demonstrated that plasmonic dipole antennas can be used to enhance the Raman signal of molecules present in the vicinity of a dipole antenna. A factor of up to 4.5 for antenna with a gap of 9 nm with an homogeneous coating of the sample with BCB molecules and an illumination source having a wavelength of 632.8 nm was measured. Even if simulations report a maximum field enhancement in the range of $10^5$ for dipole antennas excited by a 632.8 nm in the hotspot of the antenna, the real Raman enhancement depends mainly on the distribution of the molecules and was estimated to be 12 for a uniform distribution of molecules with a Gaussian illumination centered in the gap of the antenna with a gap size of 10 nm and a radius of 500 nm. This factor drops to 6.5 for an illumination radius of 700 nm.
The factor of 4.5 is in agreement with simulations performed with a defocus between 200 and 300 nm.

Molecules present in the hot spots of the antenna are also expected to deteriorate quickly reducing thus the measured Raman enhancement value. Measurements performed on molecules directly bounded to the antenna are expected to give a much higher field enhancement due to their close proximity. In this case the molecules can also dissipate the received heat through the antenna due to their direct binding. Unfortunately redeposition of substrate material during the fabrication process of the dipole antennas prevented the molecules to bind with the antenna. However, we believe that the redepositions can be removed by a wet etching step of the sample in hydrofluoric acid.
Chapter 7

Conclusions and Outlook

7.1 Summary

We demonstrated for the first time that dipole antennas with gap sizes below 5 nm can be fabricated in a reproducible way by a combination of electron beam lithography (EBL) and helium focused ion beam (He-FIB) milling. We demonstrated experimentally and by simulations that antennas with small gap sizes can achieve a higher electrical field enhancement and a higher sensitivity to effective refractive index changes of the environment in close vicinity of the antenna. An increase of the sensitivity of antennas with smaller gap sizes, up to values of $\approx 250$ nm per refractive index unit was demonstrated. This fabrication process was shown to be affected by redeposition of substrate material on top of the antenna. This effect has two main consequences. First, the resonance wavelength of the antenna is shifted towards the infrared due to its loading with dielectric material. Second, the antenna is covered by a thin layer of substrate material which was demonstrated to be sufficient to prevent the chemical binding of the thiol group of molecules with the antenna.

We presented a novel fabrication technique to produce nanostructures on polydimethylsiloxane (PDMS) using a conventional patterning method, such as electron beam lithography, on a hard substrate followed by a transfer of the structures from the hard substrate onto the PDMS. The gap size of the obtained structures can be tuned by mechanical stretching of the flexible substrate. Antenna produced with this technique have demonstrated a tuning capability of the resonance wavelength of the antennas of -0.81 nm per strain percent applied to the substrate. The tuning capability of the antennas was optimized to about -3 nm per strain percent by the introduction of pillars under the antennas. Those pillars were made
of polymethylmethacrylate (PMMA) which showed several problems. First, crack formation and unwanted scattering arose from the PMMA during stretching. Second, PMMA is very soluble in solvents, such as acetone and isopropanol, and restricts the applications in which the antennas can be implemented.

We demonstrated that optical antennas can be successfully used to enhance the Raman signal of molecules in close vicinity of the antenna. The Raman enhancement factor was measured to be about 4 for dipole antennas having a gap size of 17 nm with an homogeneous coating of the substrate with brilliant cresyl blue molecules. This enhancement factor can be considerably increased when the resonance wavelength of the antenna matches the wavelength of the incident beam. For example dipole antenna having a gap size of 3.5 nm were demonstrated by simulations to provide a Raman enhancement factor of $4.5 \cdot 10^6$ with a laser illumination at 785 nm with molecules present only on the antenna.

We believe that the combination of the two demonstrated technologies, i.e. the fabrication of antennas with sub-5 nm gap size and the fabrication of those antennas on a flexible substrate can be combined efficiently to provide a device capable of performing Raman measurements with a high achievable Raman enhancement factor. In order to achieve such a device two main aspects should be further optimized. First, antennas with pillars have to be fabricated with a better material than PMMA. Second, the gap opening by He-FIB should be further improved for antennas on PDMS substrates.

### 7.2 Outlook

We believe that the redeposition which occurs during He-FIB milling can be used favorably to protect antennas made of material which oxidizes easily in air such as silver. Silver has much less losses at optical frequencies than gold and is expected to result in a higher electric field enhancement. The second advantage is that the resonance wavelengths of silver antennas are blue shifted compared to gold. This will allow to keep the resonance wavelength of antennas in the visible range even for the ones with small gaps. Redepositions can be problematic for Raman measurements. However, we believe that they can be removed by a wet etching step of the sample in hydrofluoric acid. This etching step is also expected to create a slight undercut under the antennas which is expected to improve its local field enhancement and thus its Raman enhancement capability. With this method, the chemical binding of thiol groups of molecules onto the antenna would be possible which is expected to improve the
Raman enhancement by several orders of magnitudes.

We believe that the fabrication technique to produce antennas on PDMS can be slightly adapted to replace the PMMA layer, used for the pillars, with another material that is more resistant to solvents and strain. Polyimide might be an interesting material to investigate as it is flexible, resistant to heat and chemicals. We believe that this material would avoid, or at least reduce, the crack formation and would make the antennas compatible with the usage of solvents. This would allow the Raman measurement of molecules deposited on tunable antennas and thus to adjust the resonance frequency of the antenna according to the wavelength of the laser and of the Raman peaks.
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Appendix A

Fabry-Perot

In this chapter the calculation of the wave propagation through a 3-layer system is derived (see Figure A.1). Before going into the detail of the Fabry-Perot calculation itself, we first have a look at a 2-layer system for the case of an $s$- and $p$-polarization. In this whole chapter we will use the convention that a monochromatic wave propagating in the $x$-direction can be expressed as

$$E(x) = e^{-ikx}$$  \hspace{1cm} (A.1)

which is the convention used by our simulation software COMSOL.

![Figure A.1: Schematic of the propagation of an s-polarized wave into two or three media.](image)

(a) $s$-polarized propagation between two media. (b) $p$-polarized propagation between two media. (c) Fabry-Perot schematics through 3 different layers.

In this chapter we will be interested mainly in light linearly polarized in the $x$-direction for
the s-polarization and in the $x/z$ plane for the $p$-polarization. The wave vectors $k$ refer to the free-space values. i.e.:

$$k = \frac{2\pi}{\lambda}$$  \hspace{1cm} (A.2)

where $\lambda$ is the free-space wavelength.

**A.1 Reflection and transmission coefficients for a s-polarized wave**

For the case of a monochromatic wave with an $s$-polarization incident ($E_i$) to an interface having a refractive index $n_1$ and $n_2$ with an angle $\theta_1$ (see Figure A.1(a)), the incident electric field can be expressed as

$$E_i(r) = \begin{pmatrix} E_i \\ 0 \\ 0 \end{pmatrix} e^{i kn_1(-y \sin \theta_1 + z \cos \theta_1)}$$  \hspace{1cm} (A.3)

**A.1.1 Reflection coefficient**

For the case of an $s$-polarization the reflection coefficient at the interface between two media having a refractive index $n_1$ and $n_2$ is

$$r_{12} = \frac{E_r}{E_i} = \frac{n_1 \cos \theta_1 - n_2 \cos \theta_2}{n_1 \cos \theta_1 + n_2 \cos \theta_2}$$  \hspace{1cm} (A.4)

one should note that

$$r_{ij} = -r_{ji}$$  \hspace{1cm} (A.5)

**A.1.2 transmission coefficient**

As for the reflection, the transmission coefficient is
A.2. REFLECTION AND TRANSMISSION COEFFICIENTS FOR A P-POLARIZED WAVE

\[ t_{12} = \frac{E_t}{E_i} = \frac{2n_1 \cos \theta_1}{n_1 \cos \theta_1 + n_2 \cos \theta_2} = 1 + r_{12} \]  \hspace{1cm} (A.6)

**A.2 Reflection and transmission coefficients for a p-polarized wave**

Similarly to the s-polarization, the case of a monochromatic wave \((E_i)\) with a \(p\)-polarization incident with an angle \(\theta_1\) to an interface having a refractive index \(n_1\) and \(n_2\) (see Figure A.1(b)) can be easily calculated using the continuity of the Maxwell’s equations.

\[
E_i(r) = E_i \begin{pmatrix} \cos \theta_1 & 0 & \sin \theta_1 \\ 0 & e^{i k n_1 (-x \sin \theta_1 + z \cos \theta_1)} \end{pmatrix}
\]  \hspace{1cm} (A.7)

**A.2.1 Reflection coefficient**

For the case of a \(p\)-polarization the reflection coefficient at the interface between two media having a refractive index \(n_1\) and \(n_2\) is

\[ r_{12} = \frac{E_r}{E_i} = \frac{n_1 \cos \theta_2 - n_2 \cos \theta_1}{n_1 \cos \theta_2 + n_2 \cos \theta_1} \]  \hspace{1cm} (A.8)

**A.2.2 Transmission coefficient**

The transmission coefficient is

\[ t_{12} = \frac{E_t}{E_i} = \frac{2n_1 \cos \theta_1}{n_1 \cos \theta_2 + n_2 \cos \theta_1} = \frac{\cos \theta_1}{\cos \theta_2} (1 + r_{12}) = \frac{n_1}{n_2} (1 - r_{12}) \]  \hspace{1cm} (A.9)

**A.3 Fabry-Perot**

The Fabry-Perot problem can be splitted in three parts. First, the solution for the reflected beam. Second, the solution for the electric field inside the layer of refracting index \(n_2\). Third, the solution for the transmitted beam into the medium \(n_3\).
A.3.1 Reflected wave

If we assume that a monochromatic wave comes from the top of the structure \(E_i\), the reflected part is a superposition of the internally reflected waves.

By taking a close look at the reflected waves, we can calculate the phase difference for the \(m\)th reflected wave branch (see Figure A.2). The important distances required to calculate the phases are \(\delta = 2d \tan \theta_2\) and \(\Delta_1 = \delta \sin \theta_1 = 2d \tan \theta_2 \sin \theta_1\).

Thus the reflection coefficient for the \(m\)th wave is:

\[
\begin{align*}
    s_m &= t_{12} \left[ r_{23} e^{-i k \left( \frac{2d n_2}{\cos \theta_2} - 2d n_1 \sin \theta_1 \tan \theta_2 \right)} \right]^m t_{21}^{-1} t_{21} \\
    s_m &= t_{12} \left[ r_{23} e^{-i k \left( \frac{2d n_3}{\cos \theta_2} - 2d n_2 \sin \theta_2 \tan \theta_2 \right)} \right]^m t_{21}^{-1} t_{21}
\end{align*}
\]

(A.10)  \hspace{1cm} (A.11)

were \(n_1 \sin \theta_1 = n_2 \sin \theta_2\) was used in order to simplify the equation.

\[
\frac{1}{\cos \theta_2} - \sin \theta_2 \tan \theta_2 = \frac{1}{\cos \theta_2} - \sin \theta_2 \frac{\sin \theta_2}{\cos \theta_2} = \frac{1}{\cos \theta_2} (1 - \sin^2 \theta_2) = \cos \theta_2
\]

(A.12)  \hspace{1cm} (A.13)  \hspace{1cm} (A.14)

![Figure A.2: Close look at the first reflection and transmission in a Fabry-Perot setup](image)

\[z\]
\[0\]
\[-d\]
Now the reflection taking into account all the reflected waves can be expressed as follow (for non absorbing materials):

\[
rfp = r_{12} + t_{12} t_{21} e^{-2i k n_2 d \cos \theta_2} r_{23} \sum_{m=0}^{\infty} \left( r_{21} r_{23} e^{-2i k n_2 d \cos \theta_2} \right)^m
\]

(A.15)

\[
= r_{12} + \frac{t_{12} t_{21} r_{23} e^{-2i k n_2 d \cos \theta_2}}{1 - r_{23} r_{21} e^{-2i k n_2 d \cos \theta_2}}
\]

(A.16)

for the case of the \( n_2 \) layer having a thickness \( d \). For notation simplification, let’s define

\[
\phi := e^{-2i k n_2 d \cos \theta_2}
\]

(A.17)

and

\[
\beta := \frac{1}{1 + r_{12} r_{23} \phi}
\]

(A.18)

Thus the reflection coefficient A.16, can be expressed with the help of equations A.5, A.17, A.18 as

\[
rfp = r_{12} + \beta \phi t_{12} t_{21} r_{23}
\]

(A.19)

### A.3.2 Field in the layer \( n_2 \)

The internal field in the layer \( n_2 \) can be decomposed into a forward propagating waves \( E_f \) going downward and a backward propagating wave going upwards.

**Forward propagating wave**

\[
E_f (r = 0) = E_i t_{12} \sum_{m=0}^{\infty} \left( r_{23} r_{12} e^{-2i k n_2 d \cos \theta_2} \right)^m = \beta t_{12} E_i
\]

(A.20)
Backward propagating wave

\[
E_b(r = 0) = E_i t_{12} r_{23} \phi \sum_{m=0}^{\infty} \left( r_{23} r_{12} e^{-2ikn_2 \left( \frac{d}{\cos \theta_2} - \delta \sin \theta_2 \right)} \right)^m
\]
(A.21)

\[
= t_{12} r_{23} \phi E_i
\]
(A.22)

The phase \( \phi \) arises because we calculate the phase after a full forward and backward reflection into the \( n_2 \) layer, i.e.: the phase at the position \((0, \delta, 0)\) is equal to

\[
e^{-ikn_2 \left( \frac{d}{\cos \theta_2} - \Delta_2 \right)} = e^{-ikn_2 \left( \frac{d}{\cos \theta_2} - \delta \sin \theta_2 \right)}
\]
(A.23)

\[
= e^{-ikn_2 \left( \frac{2d}{\cos \theta_2} - \delta \sin \theta_2 \right)}
\]
(A.24)

\[
= e^{-ikn_2 \left( \frac{2d}{\cos \theta_2} - 2\delta \tan \theta_2 \sin \theta_2 \right)}
\]
(A.25)

\[
= e^{-2ikd_n_2 \left( \frac{1}{\cos \theta_2} - \tan \theta_2 \sin \theta_2 \right)}
\]
(A.26)

\[
= e^{-2ikd_n_2 \cos \theta_2}
\]
(A.27)

\[
= \phi
\]
(A.28)

\[
= \beta
\]
(A.29)

A.3.3 Transmitted wave

Similarly to what was calculated before, the transmission coefficient is

\[
t_{fp} = t_{12} e^{-ikd \left( \frac{n_2}{\cos \theta_2} - n_3 \cos(\theta_2 - \theta_3) \right)} t_{23} \sum_{m=0}^{\infty} \left( r_{23} r_{21} e^{-2ikd_n_2 \cos \theta_2} \right)^m
\]
(A.30)

\[
= t_{12} e^{-ikd(n_2 \cos \theta_2 - n_3 \cos \theta_3)} t_{23} \sum_{m=0}^{\infty} \left( r_{23} r_{21} e^{-2ikd_n_2 \cos \theta_2} \right)^m
\]
(A.31)

\[
= \beta t_{12} e^{-ikd(n_2 \cos \theta_2 - n_3 \cos \theta_3)} t_{23}
\]
(A.32)
A.3.4 Summary

For the case of $E_i = 1$, we have for an $s$-polarization

$$E_{s,x}(r) = \begin{cases} 
    e^{ikn_1 z \cos \theta_1} + [r_{12} + \beta \phi t_{12} t_{21} r_{23}] e^{-i k n_1 z \cos \theta_1} e^{-i k n_1 y \sin \theta_1} & , z \geq 0 \\
    e^{i k n_2 z \cos \theta_2} + \phi r_{23} e^{-i k n_2 z z} \beta t_{12} e^{-i k n_2 y \sin \theta_2} & , z < 0 & z \geq -d \\
    \beta t_{12} t_{23} e^{-i k d (n_2 \cos \theta_2 - n_3 \cos \theta_3)} e^{-i k n_3 (z \cos \theta_3 - y \sin \theta_1)} & , z \leq -d 
\end{cases}$$

(A.33)

and similarly for the $p$-polarization

$$E_{p,x}(r) = \begin{cases} 
    e^{i k n_1 z \cos \theta_1} - [r_{12} + \beta \phi t_{12} t_{21} r_{23}] \cdot e^{-i k n_1 z \cos \theta_1} e^{-i k n_1 x \sin \theta_1} \cos \theta_1 & , z \geq 0 \\
    e^{i k n_2 z \cos \theta_2} - \phi r_{23} e^{-i k n_2 z z} \beta t_{12} e^{-i k n_2 x \sin \theta_2} \cos \theta_2 & , z < 0 & z \geq -d \\
    \beta t_{12} t_{23} e^{-i k d (n_2 \cos \theta_2 - n_3 \cos \theta_3)} \cdot e^{-i k n_3 (z \cos \theta_3 - x \sin \theta_1)} \cos \theta_3 & , z \leq -d 
\end{cases}$$

(A.34)

$$E_{p,z}(r) = \begin{cases} 
    e^{i k n_1 z \cos \theta_1} - [r_{12} + \beta \phi t_{12} t_{21} r_{23}] \cdot e^{-i k n_1 z \cos \theta_1} e^{-i k n_1 x \sin \theta_1} \sin \theta_1 & , z \geq 0 \\
    e^{i k n_2 z \cos \theta_2} - \phi r_{23} e^{-i k n_2 z z} \beta t_{12} e^{-i k n_2 x \sin \theta_2} \sin \theta_2 & , z < 0 & z \geq -d \\
    \beta t_{12} t_{23} e^{i k d (n_2 \cos \theta_2 - n_3 \cos \theta_3)} \cdot e^{-i k n_3 (z \cos \theta_3 - x \sin \theta_1)} \sin \theta_3 & , z \leq -d 
\end{cases}$$

(A.35)
Appendix B

Bowtie Geometry

This appendix gives the details of the geometry used in the simulations and should be useful for people who want to reproduce the simulations and skip the trigonometry calculation. Those calculations are quite easy, but might be easily subject to several mistakes leading to improper geometry and thus wrong simulations especially when a simulation performs a sweep along one geometrical parameter.

We will consider the top view of the antenna (see Figure B.1) which has an arm length $\overline{AK} = L$, a width $w$ and an appex angle $\alpha$. Two different geometries are observed. The first one is the case of a triangular antenna arm with rounded corners (see Figure B.1). In the second one, each arm is composed of three rods forming a star as shown in Figure B.2.

B.1 Triangular Bowtie Antenna

The antenna geometry is displayed in detail in Figure B.1. If $(0;0)$ is the mid point of the gap and $G_x$ the $x$-coordinate of the point $G$, then:

\[
\begin{align*}
\overline{GA} &= \frac{w}{2 \sin \left( \frac{\alpha}{2} \right)} \quad \text{(B.1)} \\
G_x &= \frac{\text{gap}}{2} - \overline{GA} + \frac{w}{2} \quad \text{(B.2)} \\
\overline{AK} &= L - \frac{w}{2} \quad \text{(B.3)} \\
\end{align*}
\]
APPENDIX B. BOWTIE GEOMETRY

The geometry can easily be constructed by a boolean union of the shapes A,B and T as described in Table B.1.

**Table B.1:** Summary of the geometrical variables used to construct a triangular bowtie antenna

<table>
<thead>
<tr>
<th>ID</th>
<th>Shape</th>
<th>Center</th>
<th>Dimension(s)</th>
<th>rotation and arc</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>∅</td>
<td>(G_x + GA; 0) (G_x + GA + L - w; (L - w) \cdot \tan \left(\frac{\alpha}{2}\right))</td>
<td>(w/2)</td>
<td>(\angle = \pi \rightarrow \frac{\pi}{2} + \frac{\pi}{4})</td>
</tr>
<tr>
<td>C</td>
<td>∅</td>
<td>(G_x + GA + L - w; (L - w) \cdot \tan \left(\frac{\alpha}{2}\right))</td>
<td>(w/2)</td>
<td>(\angle = \frac{\alpha}{2} + \frac{\pi}{2} \rightarrow 0)</td>
</tr>
<tr>
<td>T</td>
<td>polygon</td>
<td>(A; A + \frac{w}{2} \left(-\sin \left(\frac{\alpha}{2}\right) \cos \left(\frac{\alpha}{2}\right)\right); C + \frac{w}{2} \left(-\sin \left(\frac{\alpha}{2}\right) \cos \left(\frac{\alpha}{2}\right)\right); C + \left(\frac{w}{2} \cos \left(\frac{\alpha}{2}\right) \right); K)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**B.2 Star-shaped Bowtie Antenna**

The antenna geometry is displayed in detail in Figure B.2.
Figure B.2: Trigonometric representation of the star-shaped bowtie geometry used in the simulation

\[
\overline{GA} = \frac{w}{2\sin\left(\frac{\alpha}{2}\right)} \quad \text{(B.5)}
\]

\[
G_x = \frac{gap}{2} - \overline{GA} + \frac{w}{2} \quad \text{(B.6)}
\]

\[
\overline{GK} = L + \overline{GA} - \frac{w}{2} \quad \text{(B.7)}
\]

\[
\overline{KT} = \overline{GK} \cdot \tan\left(\frac{\alpha}{2}\right) \quad \text{(B.8)}
\]

\[
\overline{AC} = \frac{\overline{GK} - \overline{GA} - \frac{w}{2}}{\cos\left(\frac{\alpha}{2}\right)} \quad \text{(B.9)}
\]

\[
\overline{OY} = \frac{w}{2} \cdot \frac{TK - \overline{AC} \cdot \sin\left(\frac{\alpha}{2}\right)}{\tan \alpha} \quad \text{(B.10)}
\]

\[
\overline{EY} = w \cdot \tan\left(\frac{\alpha}{2}\right) \quad \text{(B.11)}
\]

\[
\overline{OD} = \frac{2}{\sin \alpha} - \overline{OY} \quad \text{(B.12)}
\]
The geometry of the antenna can be composed by boolean operations on simple geometry units (arc of circle, rectangle and triangle) which are presented in the table B.2. From those geometrical parameters the structure can be obtained with the following boolean operation\(^1\):

\[
((T - A) - D) \cup A \cup C \cup E \cup F \tag{B.14}
\]

<table>
<thead>
<tr>
<th>ID</th>
<th>Shape</th>
<th>Center</th>
<th>Dimension(s)</th>
<th>rotation and arc</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>○</td>
<td>(G_x + GA; 0)</td>
<td>(w/2)</td>
<td>(\angle = \pi \rightarrow \frac{\pi}{2})</td>
</tr>
<tr>
<td>B</td>
<td>○</td>
<td>(G_x + GO + GA - EY; w)</td>
<td>(w/2)</td>
<td>(\angle = -\frac{\pi}{2} \rightarrow \alpha - \frac{\pi}{2})</td>
</tr>
<tr>
<td>C</td>
<td>○</td>
<td>(G_x + GK - \frac{w}{2}; AC \cdot \sin \left(\frac{\alpha}{2}\right))</td>
<td>(w/2)</td>
<td>(\angle = \alpha + \frac{\pi}{2} \rightarrow \alpha - \frac{\pi}{2})</td>
</tr>
<tr>
<td>D</td>
<td>○</td>
<td>(G_x + GO + OD; 0)</td>
<td>(w/2)</td>
<td>(\angle = \pi \rightarrow \alpha + \frac{\pi}{2})</td>
</tr>
<tr>
<td>E</td>
<td>□</td>
<td>(G_x + GA; 0)</td>
<td>(AE \times (w/2))</td>
<td>(\angle = 0)</td>
</tr>
<tr>
<td>F</td>
<td>□</td>
<td>(G_x + GO - OY + \frac{w}{2\sin \alpha}; 0)</td>
<td>(\left(\frac{AC \cdot \sin \left(\frac{\alpha}{2}\right)}{\sin \alpha} - \frac{w}{2\tan \alpha}\right) \times w)</td>
<td>(\angle = \alpha)</td>
</tr>
<tr>
<td>T</td>
<td>polygon</td>
<td>(B; E; D; D - \frac{w}{2}\left(\sin \alpha \cos \alpha\right); B + \frac{w}{2}\left(\sin \alpha - \cos \alpha\right); B)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^1\cup\) represents the union
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