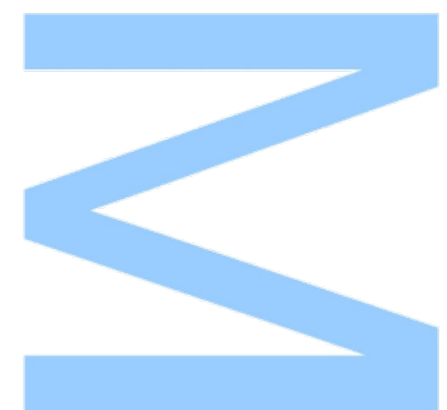
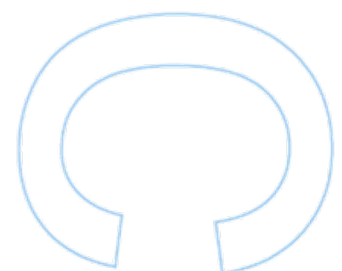
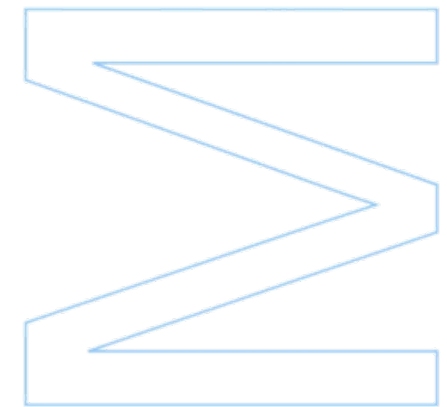
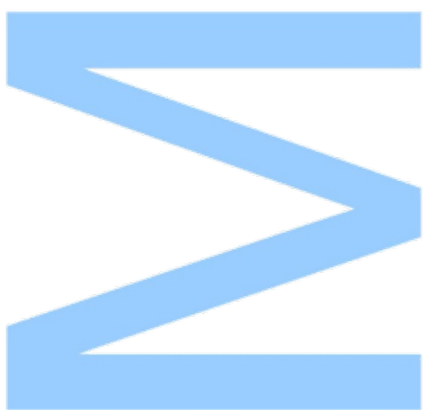


Electromagnetic Surface Waves in One Dimensional Structures: Application to Optical Sensors

Bernardo Santos Dias

Dissertação de Mestrado apresentada à
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Mestrado em Física

Departamento de Física e Astronomia

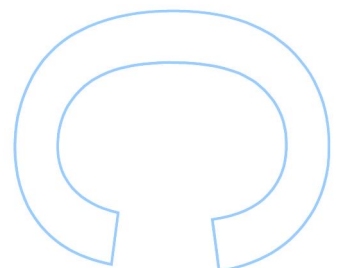
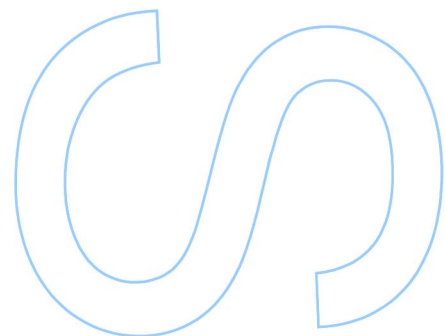
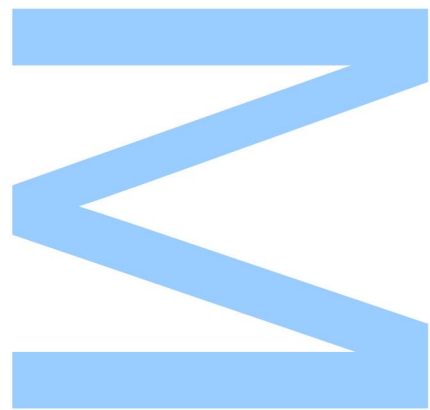
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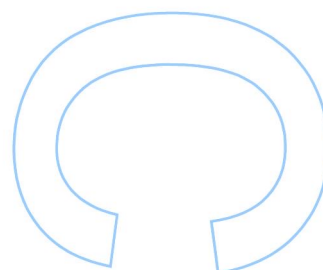
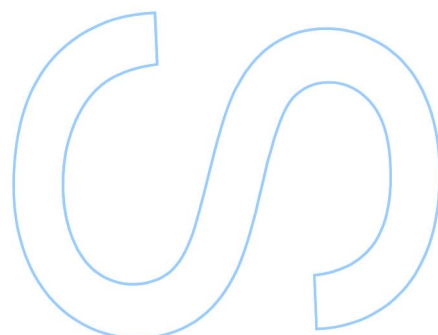
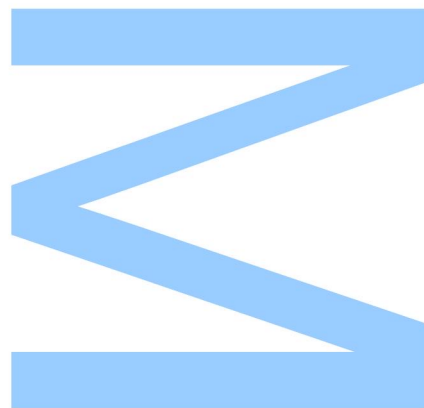




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Abstract

Electromagnetic Surface Waves (ESWs) constitute solutions to Maxwell's Equations where light is guided at the interface between two materials. These electromagnetic modes are associated with recent technological developments such as imaging setups and ultra sensitive optical sensors. Surface Plasmon Polaritons (SPPs) and Bloch Surface Waves (BSWs), which are two examples of ESWs, are generated at metal-dielectric and photonic crystal-dielectric interfaces, respectively. Both SPPs and BSWs show ideal properties for optical sensing such as large penetration depths and propagation lengths, leading to large sensitivities which are essential in surface process monitorization.

The excitation of SPPs and BSWs is experimentally studied for application in optical sensing by characterization of their refractometric sensitivity. In the case of SPPs, four different plasmonic metals (gold, silver, copper and aluminium) are tested in planar substrates, and the experimental results are compared with numerical simulations. The gold and silver SPPs are also observed in a multimode fiber configuration, contributing towards the development of cheap, portable and highly sensitive optical sensors. It is observed that silver displays an SPP mode with larger Figure of Merit due to considerably low linewidths. The sensitivity of BSWs is also characterized by comparing numerical and experimental results with a perturbation theory approach, leading to excellent agreement between all calculations. The perturbation theory approach allows an analytical description of the sensitivity of BSW modes, providing novel results for the design of photonic crystals for BSW sensing. Lastly, the simultaneous excitation of SPPs and BSWs is experimentally observed in a metal-dielectric photonic crystal, which constitutes the first observation of these modes in a single structure and may find applications in both chemical and bio sensing.

Resumo

Ondas Electromagnéticas de Supefície (OES) constituem soluções das Equações de Maxwell em que luz é guiada na interface entre dois materiais. Estes modos electromagnéticos estão associados a desenvolvimentos tecnológicos recentes como técnicas de *imaging* e sensores ópticos de elevada sensibilidade. *Surface Plasmon Polaritons* (SPPs) e *Bloch Surface Waves* (BSWs), dois exemplos de OES, são geradas em interfaces metalo-dieléctrico e cristal fotónico-dieléctrico, respectivamente. Ambos SPPs e BSWs demonstram propriedades excepcionais para sensorização óptica, como elevados comprimentos de penetração e propagação, levando a sensibilidades elevadas que são essenciais para monitorização de processos em superfícies.

A excitação de SPPs e BSWs é estudada experimentalmente para aplicação em sensorização óptica através da caracterização da sensibilidade refratométrica. No caso de SPPs, quatro metais plasmónicos (ouro, prata, cobre e alumínio) são testados, e os resultados experimentais são comparados com simulações numéricas. Os modos SPP de ouro e prata são também observados numa configuração de fibras multimodo, permitindo a fabricação de sensores de custo reduzido, portáteis e com elevada sensibilidade. Observa-se que a prata demonstra um modo SPP com elevada Figura de Mérito devido a largura a meia altura reduzida. A sensibilidade de BSWs é também caracterizada ao comparar resultados numéricos e experimentais com uma abordagem semi-analítica baseada em teoria de perturbações, conduzindo a excelente concordância entre todos os cálculos efectuados. A abordagem de teoria de perturbações permite uma descrição analítica da sensibilidade de modos BSW, reportando novos resultados relevantes para a fabricação de cristais fotónicos para sensorização baseada em BSWs. Por último, a excitação simultânea de SPPs e BSWs é demonstrada experimentalmente num cristal fotónico metalo-dieléctrico, constituindo a primeira observação simultânea destes modos numa única estrutura, e que poderá encontrar aplicações em sensores químicos e biológicos.

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Acronyms

AS	Adsorption Sensitivity	RI	Refractive Index
ATR	Attenuated Total Reflection	RS	Refractometric Sensitivity
BSE	Backscattered Electrons	SE	Secondary Electrons
BSW	Bloch Surface Wave	SPP	Surface Plasmon Polariton
ESW	Electromagnetic Surface Wave	SPR	Surface Plasmon Resonance
GMR	Guided Mode Resonance	SRSPP	Short Range Surface Plasmon Polariton
LRSP	Long Range Surface Plasmon Polariton	TH	Target Holder
PhC	Photonic Crystal	TE	Transverse Electric
PT	Perturbation Theory	TM	Transverse Magnetic
MDPhC	Metal Dielectric Photonic Crystal	TMM	Transfer Matrix Method
MMF	Multimode Fiber	TPP	Tamm Plasmon Polariton
NIR	Near Infrared	UV	Ultraviolet
NUV	Near Ultraviolet		
RF	Radio Frequency		

Chapter 1

Introduction

Electromagnetic surface waves (ESWs) consist of solutions of Maxwell's Equations corresponding to configurations in which light is guided at the interface of two different structures. While the most simple case of ESWs is guided light at the interface between two homogeneous and isotropic materials, more intricate solutions such as modes at the interface between isotropic and anisotropic materials or nonhomogeneous and homogeneous materials are also possible [1]. All of these different combinations of partnering materials give rise to different ESWs, some of which have not been experimentally demonstrated yet.

The work developed in this Master's thesis regards the experimental study of two ESWs: Surface Plasmon Polaritons (SPPs) and Bloch Surface Waves (BSWs). While both ESWs have been thoroughly studied, the predominance of SPPs in both theoretical and practical applications in the past has led to discussion among the optical sensor community regarding the fact that SPP based sensors may be reaching its theoretical limits [2]. This discussion, along with some limitations of SPP based devices, led to a renewal in the research of BSWs, which may be seen as viable alternatives for optical sensing.

Surface Plasmon Polaritons constitute surface modes excited at a single metal-dielectric interface, while BSWs are excited at the surface between a periodically nonhomogeneous dielectric (photonic crystal) and a homogeneous dielectric [1]. While BSWs constitute the basic ESW mode generated in periodic media, very interesting phenomenology is observed when creating metal-dielectric periodic structures, which leads to the interaction of SPP modes in different layers.

This chapter presents a short introduction to the work developed in this master's thesis, along with some context regarding the research group and the associated projects. Then, in Chapter 2 the theory of SPPs and BSWs is thoroughly detailed, covering not only on the physics behind these phenomena but also their application in optical sensing. The chapter ends with the description of the behaviour of metal-dielectric periodic structures. In Chapter 3, the experimental and simulations methods are detailed, providing a detailed account on the research methods behind the results obtained. These simulation and experimental results are presented

in Chapter 4, which contain two sections with novel contributions in both ESW excitation and sensing. Lastly, conclusions are drawn in Chapter 5, providing a short analysis of the work developed and a commentary on possibilities for future work.

1.1 State of the Art

Electromagnetic surface wave classification depends on the optical and geometrical properties of the structure. The first reported study of ESWs was made by Zenneck in 1907 [3], which regarded the possibility of waveguiding at the interface between the atmosphere and the Earth or a large body of water. While the existence of this wave remains controversial [1], other ESWs have been experimentally studied and observed. The first of these waves was the Surface Plasmon Polariton, which has evolved into becoming an important phenomenon in optical device design, having been applied in optical sensors [4, 5], imaging and microscopy setups [6, 7], waveguides [8, 9], resonators [10] and solar cells [11, 12]. In the case of optical sensors, the commercialization of SPR based setups by Biacore [13] led to an increase in popularity of this surface wave in applications for monitoring of surface phenomena.

The first documented observation of SPR was made in 1902 by R.W. Wood (1868-1955), who observed dark spots in the reflection spectrum of a metal backed diffraction grating [14]. While it is known today that this phenomenon corresponds to the coupling of light to the free electrons in the metal (creating an absorption peak in the spectrum), it was not understood at the time. Lord Rayleigh (1842-1919) expanded the knowledge of diffraction gratings in the coming years [15], but only in 1941, with the work of Ugo Fano (1912-2001) [16], was suggested that these dark spots correspond to a surface wave. In the 1950's David Bohm (1917-1992) and David Pines (1924-2018) suggested that the observed phenomenon was associated with plasma oscillations of the free electrons in a metal [17, 18, 19], thus casting light on the physical phenomenon behind the spectral dips observed. Finally, in the 1960's the excitation of SPR using total attenuated reflection was demonstrated in two different configurations, following the works by Kretschmann and Raether [20] and Otto [21]. These developments paved the way for technological developments of the coming decades, which evolved into the prominence of SPR in many fields of optical device design.

Current research in application of surface plasmons is mostly divided in improvement of the quality factor of the resonance, development new plasmonic materials, design of optical devices that control light at the nanometer scale and quantum plasmonics. Wang et al. [22] provided an extensive review on current mechanisms for decreasing linewidth of SPPs, which range from experimental setup improvements, such as lowering the operating temperature (which decreases electron phonon collisions and thus decreases damping) [23], or surface roughness decrease [24]; to the use of new mechanisms such as Fano resonances [25], surface lattice resonances [26], plasmonic induced transparency [27] or Tamm Plasmon-Polaritons [28]. On the other hand, the development of new plasmonic materials, which aims to reduce resonance linewidth and to present new solutions for more flexible applications, has evolved into a notable research field, with

current research ranging from development of new alloys with different optical properties [29], conductive metal oxides and nitrides [30, 31] and alternative metals such as rare earths [32, 33]. The development of ever more intricate structures at the micrometer and nanometer scale is also an active field of research, and configurations such as plasmonic trench resonators [34], plasmonic whispering-gallery microcavities [35], periodic nanoparticle arrays [36] and hypergratings [37] have been experimentally demonstrated, achieving linewidths as low as 1.11nm [38]. Lastly, in the field of quantum plasmonics, many research paths are being taken, which range from the theoretical description of quantum effects [39, 40], development of new devices such as single photon sources [41, 42], subnanometer gap structures [43] or optoelectronic switching [44]. In particular, the development of quantum nanoplasmonic platforms for sensing shows great promise in attaining the limit of single molecule detection [45] by breaking the quantum noise limit [46], thus providing new generation ultra-sensitive plasmonic devices.

The commercialization of the first SPP based sensors increased significantly the popularity of the method for surface process monitoring [47], which now is one of the standard approaches in experimental surface chemistry [48]. While in the early 1980's to early 2000's the foundations behind SPR sensors were laid [49, 50], the forty years of intensive research have led to the development of devices with extreme sensitivity, and current paths of research focus mostly on the development of nanostructures and combination with novel materials that maximize sensitivity [5]. Regarding the development of novel SPR sensor nanostructures, the focus of research is shared with many other plasmonic research fields in the search for high quality factor resonances, design flexibility and extreme sensitivity. Sensitivities up to 25000 nm/RIU have been reported in a grating structure [51] and 10280 nm/RIU in a fiber optics configuration [52]. On the other hand, while gold is still the standard in SPR based sensing due to oxidation resistance and chemical compatibility with known surface binding processes [48], research into the combination of plasmonic metals with graphene [53], black phosphorus [54], molybdenum disulfide [53] or oxidation resistant dielectrics [51] have led to the development of more flexible SPR sensors, which may fit aggressive environments and significantly lower the production cost of SPR based sensors.

In the 1970's, with the research efforts put into propagation of light in photonic crystals (PhC), a second type of ESW was discovered. This ESW, which propagates in the interface between a PhC and a uniform dielectric, is called a Bloch Surface Wave. The first description of this wave was provided by Yeh, Yariv and Hong in 1976 [55], who studied propagation of light in periodic media. Experimental observation of this ESW was reported in 1978 by the same authors, using a GaAs-AlGaAs multilayer stack grown by molecular-beam epitaxy [56].

Propagation of light in periodic media shares many similarities with the propagation of electrons in crystals, because Bloch's Theorem is applicable in both cases. The analogy between the two fields runs even deeper with the fact that electronic Tamm states, which are surface states generated by the truncation of a crystal [57], are also present in PhCs in what are called optical Tamm states or Bloch surface waves [58].

An interesting observation regarding this ESW is that while SPPs gained considerable

popularity during the 1980's, BSWs remained a much less popular topic until the late 1990's, where the properties of this wave were experimentally studied [59, 60]. This focus led both theoretical [61, 62] and the proposal of the first BSW based optical devices [63, 64]. Current fields of research include optical sensors [65, 66, 67, 68], optical manipulation [69, 70], surface optics [71, 72] and waveguiding [67, 73]. In the case of optical the similarity between BSWs and SPPs has drawn comparisons between the two [74, 75, 76]. While SPPs generally display much higher sensitivities, BSWs may have other advantages such as durability associated with dielectric stacks [77], chemical and mechanical stability [76] and design flexibility due to a large number of available materials.

Current research into BSW based sensors regards the optimization of devices, developing new sensing schemes, integration in compact and flexible optical devices and compatibilization with known surface functionalization procedures. Regarding the optimization of BSW based sensors, focus has been placed on both the maximization of the sensitivity and FoM, either by studying the dependence of these metrics with the incident angle [78], dependence on the layer thicknesses and optical properties [79] and dependence with layer absorption [75, 80]. Gryga et al. developed a sensing scheme based on the ratio of reflectances of different polarizations, allowing the visualization of a clear reflection band even in very low pronounced BSW peaks [76]. This method allowed the fabrication of several BSW based sensors, having already proven concepts in refractometric [81], gas [82] and relative humidity sensing [83].

Integration of BSW devices in flexible platforms has also been an important focus of research, following a similar path to that of SPP based sensors. As such, the integration in optical fibers has been an important area of research, with the concept demonstrated on photonic crystal fibers [84], D-shaped single mode fibers [67], optical fiber tips [85] and a tapered single mode fiber [86]. Such devices show more flexibility due to the absence of a prism and are considerably cheaper, thus being a promising candidate for real world application of BSW sensors.

Application of BSW based sensors in bio and chemical sensing has also seen a large number of contributions, which take advantage of the sharp modes displayed in the reflectance spectrum. Through proper surface functionalization, BSW sensors have been demonstrated to detect cancer biomarkers [87], the Hepatitis B virus [88] and to monitor the binding kinetics of antibodies to living bacteria [89]. Biosensing using BSWs has also seen interesting development using imaging techniques, allowing the monitorization of different ligands immobilized in small spots with sub-picogram resolution [90, 88].

While these both SPPs and BSWs are studied in this work, other surface modes have also been reported theoretically and experimentally. The first of these waves are Tamm Plasmon Polaritons (TPPs), which are generated at the interface between a PhC and a metal layer. These ESWs were first reported theoretically [91, 28], and first demonstrated in 2010 [92]. The application of TPPs in optical sensors has also been reported [93, 94], although since the wave is not generated at an interface with the analyte special implementations such as porous materials are needed [95] for high sensitivities. More complicated phenomena, such as Dyakonov waves [96], Dyakonov Voigt [97] and Dyakonov Tamm waves [98] have also been reported, which use anisotropic materials in

at least one of the interfaces, thus presenting considerably larger experimental difficulties for their practical implementation.

1.2 Electromagnetic Surface Waves in Periodic Media

The study of the effects resulting from interactions in periodic systems is a central problem not just in Condensed Matter Physics (where the electron dynamics in periodic lattices is of great importance) but also in Nanophotonics. It is interesting to observe that the same phenomenology is present for specific types of systems no matter the field within physics. One example is the formation of allowed bands (and consequently, of BSWs) in PhCs, which stems from the interaction of guided modes within different waveguiding layers, leading to a splitting process which creates a propagation band. While this process is at the heart of BSW formation, very similar phenomenology happens when SPPs are considered in periodic media. In this case, a similar splitting process is observed, leading to the creation of a plasmonic band with highly desirable properties such as possibilities of extreme confinement and negative refraction [99]. Avrutsky et al. argue that this splitting process is a universal phenomenon associated with linear wave dynamic systems, being also present in quantum mechanics, acoustics and AC circuits [100].

Much interest has been demonstrated in the combination of metal films with PhCs due to their ability to simultaneously support guided and plasmonic modes, thus being called metal-dielectric photonic crystals (MDPhCs) or plasmonic crystals. While the research in conventional PhCs, which stems from the 1970s and 1980s, seems to be reaching its limits [101], the incorporation of plasmonic modes in periodic structures is a very active field of research, allowing the inclusion of effects beyond the diffraction limit and, in particular by including electronic resonances.

In the past decade, the incorporation of metals into traditional photonic crystal structures has been a research focus, in order to combine typical photonic and electronic resonances in a single device. One of the main ways of integrating metals in PhCs is to include a metal film above or below a PhC, which has been done in 1D [102, 103], 2D [104], 3D [105, 106] structures. The advantages sought in this integration of a metal layer are the creation of an omnidirectional PhC band gap [101] (which happens due to the high RI contrast between metal and dielectric), improving lasing [107], increasing mode confinement, and resonance tuning by controlling the metal fill fraction [108].

In the case of optical sensors, much attention has been given to these structures due to the search for improvement of typical SPR sensors. A particularly researched configuration has been the inclusion of a metal film on top of a 1D PhC [109, 110, 111, 102, 103], creating highly sensitive, ultralong range SPPs which may outperform conventional metal on dielectric SPP configurations. Other configurations, such as nanoparticle arrays or metals on opal structures have also been reported for sensing purposes [112, 113].

When the size of the MDPhC cell is considerably smaller than the operating wavelength and diffractive effects are no longer present, light enters the realm of metamaterials. A special

type of metamaterials, which are produced by the inclusion of metals in the unit cell, are called hyperbolic metamaterials (HMMs). HMMs constitute an active field of research due to very interesting properties displayed by these materials, which range from enhanced spontaneous emission [114, 115], negative refraction [116], and spacetime phenomena [117]. In the case of optical sensors, research in HMMs has led the demonstration of devices with extremely high sensitivities, which may revolutionize the sensing paradigm. Using a 2D nanorod HMM, Kabashin et al. developed an optical sensor showing sensitivities near 32000 nmRIU^{-1} , allowing detection of biotin molecules in very low concentrations [118]. Sreekanth et al. developed an HMM based sensor that allows excitation of high-k modes using a hypergrating, achieving sensitivities of 30000 nmRIU^{-1} [119], also demonstrating its application in detection of thrombin [120]. These sensors display remarkable sensitivities, but require specialized equipment for fabrication. Recently, Gao et al. developed an $\text{Ag}/\text{TiN}_x\text{O}_y$ layered film HMM for refractometric sensing [108], which allows excitation of SPR using a conventional BK7 prism under the Kretschmann configuration, and displaying a sensitivity of $2475.20 \text{ nm RIU}^{-1}$.

1.3 Context of the work

The work developed in this Master's thesis is integrated in *SurfWave*, a research project supported by Instituto de Engenharia de Sistemas e Computadores, Tecnologia e Ciência (INESC TEC). The main purpose behind the project is to develop new BSW based solutions for optical sensing, with an ultimate goal of developing a fully functioning prototype for thrombin detection. Within the objectives of the project are the development of the experimental methods for PhC deposition, a setup for ESW characterization and software for simulations of the PhC spectra. The work developed to achieve these goals is reported in the following chapters.

The project builds upon previous knowledge within the research group, which has specialized in the development of SPP based optical sensors. The new research path into BSWs aims to provide more flexible solutions, which will find application where many SPP based sensors fail, such as extreme or corrosive environments. With this work, the author hopes to establish a foundation which can be built upon for the development of state of the art solutions in optical sensing.

Chapter 2

Electromagnetic Surface Waves

The behaviour of electromagnetic waves incident on a 1D multilayer structure stems down to simple phenomena such as refraction and reflection at different interfaces, and phase shifts within the layers. Nevertheless, the combination of these phenomena along with light-matter interactions give rise to the emergence of complex behaviour even in very simple structures such as metal dielectric interfaces. Such an example are electromagnetic surface waves, which depend both on the characteristics of the incident light and the optical properties of the materials considered. When correctly designed, optical devices can manipulate light by taking advantage of these phenomena, which may range from everyday applications (such as optical filters and coatings) to extremely precise control of sub-micron interactions in laboratory context.

The propagation of light in 1D layered media can be accurately described by using the Transfer Matrix Method [121, 122], which takes advantage of the linearity of the fields between layers and provides a simple matricial formalism in which 1D phenomena can be described, from reflection spectra to dispersion relation calculations. As such, the chapter begins with a derivation of this formalism directly from Maxwell's Equations, and will form the basis for both the theoretical and the simulation calculations here presented. Using the TMM formalism, the properties of SPPs and BSWs are derived and their application to optical sensing is studied. The same formalism is used to derive the physics behind MDPHCs, allowing the study of these structures that may present both SPP and BSW modes.

2.1 Propagation of Light in 1D Layered Media

2.1.1 From Maxwell's Equations to the Transfer Matrix Method

The description of light propagation comes from Maxwell's Equations, which form the basis of Electromagnetism. Consider the source-free Maxwell's Equations [123]:

$$\nabla \cdot \vec{E} = 0 \quad (2.1a)$$

$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad (2.1b)$$

$$\nabla \cdot \vec{B} = 0 \quad (2.1c)$$

$$\nabla \times \vec{B} = \mu\epsilon \frac{\partial \vec{E}}{\partial t} \quad (2.1d)$$

In Equations 2.1, $\vec{E}$ is the electric field, $\vec{B}$ is the magnetic induction field, t represents time, and ϵ and μ are rank 2 tensors called the permittivity and permeability of the material, which reduce to a scalar in isotropic materials (which we will consider). The fields are connected by the constitutive relations, which for linear, non magnetic materials, are expressed as [123]

$$\vec{D} = \epsilon \vec{E}, \quad \vec{B} = \mu_0 \vec{H} \quad (2.2)$$

where $\vec{D}$ is the electric displacement field, $\vec{H}$ is the magnetic field. On the other hand, $\mu_0 = 4\pi \times 10^{-7} \text{H/m}$ is the permeability of vacuum. By combining the curl equations 2.1b and 2.1d along with the constitutive relations 2.2, one obtains:

$$\nabla \times (\nabla \times \mu_0 \vec{E}) + \epsilon \frac{\partial^2 \vec{E}}{\partial t^2} = 0 \quad (2.3)$$

Notice that the same process can be done for $\vec{H}$, obtaining a similar equation to 2.3. By applying the vector identity $\nabla \times (\nabla \times) = \nabla(\nabla \cdot) - \nabla^2$ and Equation 2.1a, the standard electromagnetic wave equations are obtained:

$$\nabla^2 \vec{E} - \mu_0 \epsilon \frac{\partial^2 \vec{E}}{\partial t^2} = 0, \quad \nabla^2 \vec{H} - \mu_0 \epsilon \frac{\partial^2 \vec{H}}{\partial t^2} = 0 \quad (2.4)$$

Equation 2.4 has solutions that take the form of monochromatic plane waves [123], which can be written as

$$\begin{aligned} \vec{E}(\vec{r}, t) &= \vec{E}_0 \exp\{\vec{k} \cdot \vec{r} - \omega t\} \\ \vec{H}(\vec{r}, t) &= \vec{H}_0 \exp\{\vec{k} \cdot \vec{r} - \omega t\} \end{aligned} \quad (2.5)$$

where $\vec{E}_0$ and $\vec{H}_0$ define the field amplitude and direction, ω is the angular frequency of the field's oscillation, $\vec{r}$ is the position vector and $\vec{k}$ is the wavevector.

Consider the incidence of polarized light on an interface between two materials of permittivity ϵ_1 and ϵ_2 , as illustrated in Figure 2.1. The superscript $+$ ($-$) indicates propagation in the positive (negative) z direction.

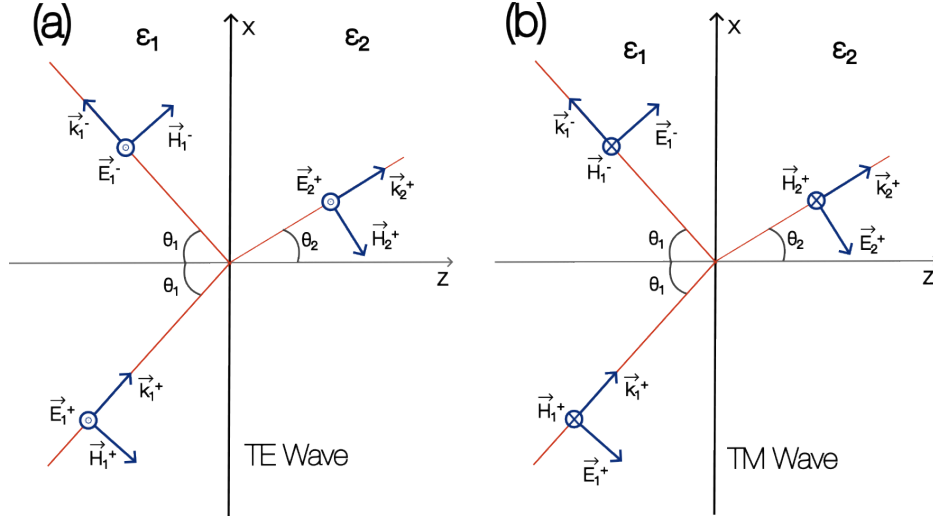


Figure 2.1: Reflection and transmission of electromagnetic waves at an interface between two materials: a) TE wave (s polarization); b) TM wave (p polarization). An incident wave with amplitudes (E_1^+, H_1^+) is partially reflected and transmitted at the interface.

In both cases, an incident wave with amplitudes (E_1^+, H_1^+) (the subscript indicates the medium) is partially reflected and transmitted, originating a reflected wave with amplitudes (E_1^-, H_1^-) and (E_2^+, H_2^+) , respectively. For brevity, consider only the TM case (Figure 2.1 (b)), while the TE case can easily be obtained analogously. The electric field has two components (x and z), while the magnetic field has only one component (y):

$$\vec{E} = (E_x, 0, E_z), \quad \vec{H} = (0, H_y, 0) \quad (2.6)$$

Given the continuity of the tangential components of the fields, which must match at both sides of the interface [123], from Figure 2.1 it is clear that:

$$H_{1y}^+ + H_{1y}^- = H_{2y}^+, \quad E_{1x}^+ + E_{1x}^- = E_{2x}^+ \quad (2.7)$$

By combining Equation 2.7 along with the plane wave basis (Equation 2.5), Maxwell's Equations (Equations 2.1) and the constitutive relations (Equations 2.2), one obtains:

$$\vec{k} \times \vec{H} = -\frac{\varepsilon_1 \omega}{c} \vec{E} \quad (2.8)$$

By using Equation 2.6 in Equation 2.8 and separating along incident and reflected components, one obtains:

$$\varepsilon_1 \omega E_{1x}^+ = k_{1z} H_{1y}^+, \quad \varepsilon_1 \omega E_{1x}^- = -k_{1z} H_{1y}^- \quad (2.9)$$

and a similar relation for the field in the second medium. Inserting Equation 2.9 into the electric field continuity (Equation 2.7):

$$\frac{\varepsilon_1 \omega}{k_{1z}} E_{1x}^+ - \frac{\varepsilon_1 \omega}{k_{1z}} E_{1x}^- = \frac{\varepsilon_2 \omega}{k_{2z}} E_{2x}^+ - \frac{\varepsilon_1 \omega}{k_{2z}} E_{2x}^- \quad (2.10)$$

Equation 2.10 can be cast in matrix form, using the components that propagate in each direction as the vector entries. After recasting in matrix form and doing some algebra, it can be shown that [121]:

$$\begin{pmatrix} H_2^+ \\ H_2^- \end{pmatrix} = \mathbf{M}^P \begin{pmatrix} H_1^+ \\ H_1^- \end{pmatrix}, \quad \mathbf{M}^P = \frac{1}{2} \begin{pmatrix} 1 + \frac{\varepsilon_2 k_{1z}}{\varepsilon_1 k_{2z}} & 1 - \frac{\varepsilon_2 k_{1z}}{\varepsilon_1 k_{2z}} \\ 1 - \frac{\varepsilon_2 k_{1z}}{\varepsilon_1 k_{2z}} & 1 + \frac{\varepsilon_2 k_{1z}}{\varepsilon_1 k_{2z}} \end{pmatrix} \quad (2.11)$$

For the case of TE polarization, an identical formulation can be found analogously, leading to:

$$\begin{pmatrix} E_2^+ \\ E_2^- \end{pmatrix} = \mathbf{M}^s \begin{pmatrix} E_1^+ \\ E_1^- \end{pmatrix}, \quad \mathbf{M}^s = \frac{1}{2} \begin{pmatrix} 1 + \frac{k_{1z}}{k_{2z}} & 1 - \frac{k_{1z}}{k_{2z}} \\ 1 - \frac{k_{1z}}{k_{2z}} & 1 + \frac{k_{1z}}{k_{2z}} \end{pmatrix} \quad (2.12)$$

Equations 2.11 and 2.12 allow one to describe the phenomenon of reflection and refraction at an interface between two materials. By using the interface matrix $\mathbf{M}$, the field amplitudes in the next layer can be easily related to the fields in the previous layer. In order to produce a description which is polarization independent, we shall adopt the variable Ψ for the fields, which represents the tangential component of the electric or magnetic fields (in this case, the y component) depending on which polarization is meant.

Consider now a multilayer structure, illustrated in Figure 2.2.

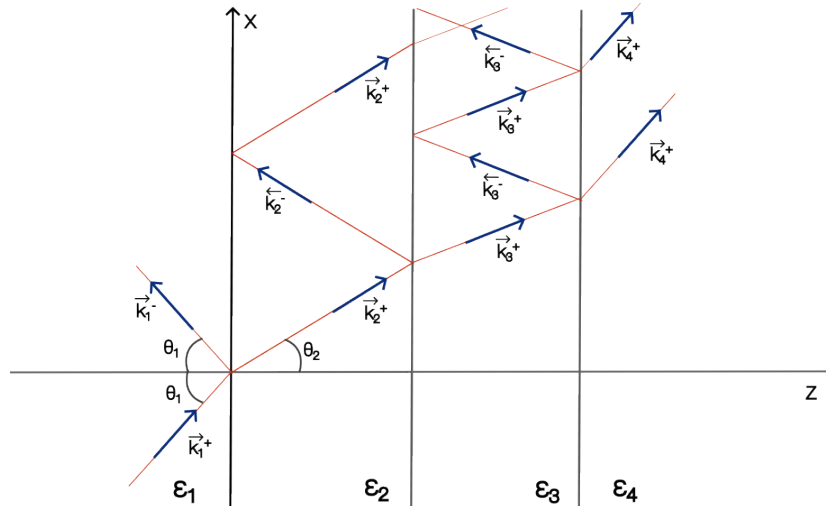


Figure 2.2: Propagation of light inside a 1D four layer structure. Notice how in each interface the field inside will be given by a sum of forward and backward propagating waves, resulting from multiple reflection and transmission instances.

In order to describe a structure such as that of Figure 2.2, one needs to account for the multiple interfaces as well as the propagation inside each layer, which adds a phase to the wave. Thus, it is possible to describe the propagation inside a material in the TMM formalism as

$$\mathbf{P} = \frac{1}{2} \begin{pmatrix} \exp\{ik_{jz}d\} & 0 \\ 0 & \exp\{-ik_{jz}d\} \end{pmatrix} \quad (2.13)$$

where d refers to the layer thickness and k_{jz} is the normal (z) component of the wavevector in the j th layer, given by $k_{jz} = \sqrt{(\omega/c)^2 \varepsilon_j - k_1 \sin \theta_1}$. Equations 2.12, 2.11 and 2.13 allow for the calculation of the optical properties of any layered structure simply by accounting all the interfaces and internal propagation inside each layer. As such, the transfer matrix of a 1D optical structure such as the one in Figure 2.2 can be written as (where the subscripts indicate the medium):

$$\begin{pmatrix} \Psi_n^+ \\ \Psi_n^- \end{pmatrix} = \mathbf{M}_{1,2} \mathbf{P}_2 \mathbf{M}_{2,3} \mathbf{P}_3 \dots \mathbf{M}_{n-1,n} \begin{pmatrix} \Psi_1^+ \\ \Psi_1^- \end{pmatrix} = \prod_{i=1}^n \mathbf{M}_{i,j} \mathbf{P}_j \begin{pmatrix} \Psi_1^+ \\ \Psi_1^- \end{pmatrix} = \mathbf{M} \begin{pmatrix} \Psi_1^+ \\ \Psi_1^- \end{pmatrix} \quad (2.14)$$

As will be seen in the next section, Equation 2.14 allows for a simple method to calculate the properties of stacks of materials (given the RI and thicknesses of each layer), whether they are composed of dielectrics or metals. The reflectivity, transmission and absorption spectra, as well as dispersion relations and existence of bound modes can be easily calculated numerically by performing matrix multiplications, which can be implemented computationally. As such, this formulation of light propagation will play a central role in the work presented, both in analytical and numerical results.

2.1.2 Optical Properties of Multilayer Stacks with the Transfer Matrix Method

Transmission, Reflection and Absorption

Consider the system of Figure 2.2 with transfer matrix $\mathbf{M}$, in which an incident wave of amplitude Ψ_1^+ is both reflected and transmitted by the structure, generating a backwards propagating wave of amplitude Ψ_1^- and a forward propagating wave of amplitude Ψ_n^+ . The reflection and transmission amplitudes for the fields can be defined as [121]:

$$r \equiv \frac{\Psi_1^-}{\Psi_1^+} \quad t \equiv \frac{\Psi_n^+}{\Psi_1^+} \quad (2.15)$$

Writing r and t as functions of the transfer matrix properties is a simple task. In the matrix formalism, it is possible to describe the system of Figure 2.2 as:

$$\begin{pmatrix} \Psi_n^+ \\ 0 \end{pmatrix} = \mathbf{M} \begin{pmatrix} \Psi_1^+ \\ \Psi_1^- \end{pmatrix} \quad (2.16)$$

Combining Equations 2.15 and 2.16, one can easily obtain an expression for the reflection coefficient:

$$r = -\frac{M_{21}}{M_{22}} \quad (2.17)$$

Similarly, the transmission amplitude can be written as:

$$t = \frac{M_{11}M_{22} - M_{12}M_{21}}{M_{22}} = \frac{\det \mathbf{M}}{M_{22}} \quad (2.18)$$

When performing optical measurements, the reflectance or transmittance (power per unit area) are generally measured. Similarly to the definition of the transmission and reflection amplitudes (defined as ratios of the field in two different media, Equation 2.15), the reflectance and transmission can be analogously defined as ratios of energy flow in two different media [121]. Considering the optical fields are harmonic regarding the time dependence, the averaged Poynting vector over one period is defined as $\vec{S} = \frac{c}{8\pi} \text{Re}\{\vec{E} \times \vec{H}^*\}$, one can write the perpendicular component of the vector (energy flow perpendicular to the interface) as:

$$S_{1z} = \frac{c}{8\pi} \text{Re}\{E_{1x}H_{1y}^{+*}\} = \frac{c^2}{8\pi} \frac{\text{Re}\{k_{1z}\}}{\varepsilon_1\omega} |H_{1y}^+|^2 \quad (2.19)$$

where in the last equality Equation 2.8 was used. An analogous expression is obtained for the energy flow in the n th medium. Thus, the reflectance of a single interface can be defined as:

$$R \equiv \frac{S_1^-}{S_1^+} = \frac{|\Psi_{1y}^-|^2}{|\Psi_{1y}^+|^2} = |r|^2 = \left| \frac{M_{21}}{M_{22}} \right|^2 \quad (2.20)$$

The final equality of Equation 2.20 is valid for both s and p polarizations. In the case of transmittance, a dependence in light polarization can be found:

$$\begin{aligned} T^p &\equiv \frac{S_n^+}{S_1^+} = \frac{\varepsilon_1}{\varepsilon_n} \frac{\text{Re}\{k_{nz}\}}{\text{Re}\{k_{1z}\}} |t|^2 = \frac{\varepsilon_1}{\varepsilon_n} \frac{\text{Re}\{k_{nz}\}}{\text{Re}\{k_{1z}\}} \left| \frac{\det \mathbf{M}}{M_{22}} \right|^2 \\ T^s &\equiv \frac{S_n^+}{S_1^+} = \frac{\text{Re}\{k_{nz}\}}{\text{Re}\{k_{1z}\}} |t|^2 = \frac{\text{Re}\{k_{nz}\}}{\text{Re}\{k_{1z}\}} \left| \frac{\det \mathbf{M}}{M_{22}} \right|^2 \end{aligned} \quad (2.21)$$

It can be shown that in the case of just the interface between two dielectric materials Equations 2.20 and 2.21 reduce to the Fresnel reflection and transmission power coefficients [121]. These equations play a central role in the simulations implemented, given that in the experimental setup devised the reflectance or optical density (absorbance) are measured, meaning that these

equations can be used for a calculation of the optical structure's spectrum and be directly compared with experimental data.

In the absence of losses, the perpendicular components of the wavevector to the interface are real and it can be easily showed that $T + R = 1$. In the case of the inclusion of lossy materials (such as metals) the wavevectors carry an imaginary component associated with the absorption of the material, and $A = 1 - (T + R)$, where A is the absorptance of the structure.

Bound States in Optical Structures

Consider an n -layered optical structure, such as the one illustrated in Figure 2.2. In such a structure, two classes of solutions to Maxwell's Equations arise [122]. First of all, the structure may present guided modes, which consist of field configurations that propagate inside the structure and decay exponentially outside of it. On the other hand, ESWs may also be present, which are characterized by an exponential decay in both sides of an interface. In the case of ESWs, this interface is the boundary between two different materials, while in the case of guided modes the interfaces consist of the boundary of the waveguide with the exterior medium. Guided modes are similar to the solutions of the particle in a box model of Schrödinger's Equation, in which the wavefunction also decays exponentially in both sides of the potential well [121].

In the transfer matrix formalism, an easy condition can be derived to verify whether a bound state (ESW or guided mode) exists. Firstly, the field is required to decay exponentially on both sides of the interfaces of the optical device:

$$\begin{aligned}\Psi_1^- &\propto \exp\{-\kappa x\}, & x < 0 \\ \Psi_n^+ &\propto \exp\{\kappa x\}, & x > L\end{aligned}\tag{2.22}$$

where κ is the decay constant and is a real positive number and L is the thickness of the structure. In this case, the fields on the incoming directions are set to zero to avoid configurations that increase exponentially far away from the interface, so $\Psi_n^- = \Psi_1^+ = 0$. Writing this field configuration in the matrix formalism, one obtains:

$$\begin{pmatrix} \Psi_n^+ \\ 0 \end{pmatrix} = M \begin{pmatrix} 0 \\ \Psi_1^- \end{pmatrix}\tag{2.23}$$

From Equation 2.23 the condition for existence of bound states can be obtained:

$$M_{22} = 0\tag{2.24}$$

From Equation 2.24 it is possible to determine not only the existence of bound states but also it's dispersion relation, both numerically and analytically (for very simple systems). For this reason, this relation will be used in the next chapters to analitically determine the

dispersion relation of ESWs, such as the surface plasmon polariton (dielectric metal interface) and the Bloch surface wave (photonic crystal - dielectric interface). At the same time, for more complicated systems (which also include guided modes or more complicated ESW's), a numerical implementation of Equation 2.24 can be made, allowing a computational calculation of the dispersion relation of the modes associated with an optical structure.

2.2 Surface Plasmon Polaritons

Given the transfer matrix approach previously presented, we now move on to the study of ESWs, in particular modes sustained at the interface between a metal and a dielectric - Surface Plasmon Polaritons (SPPs). This section presents the basic theory of SPPs, deriving the properties of this ESW from the TMM formalism (allowing the calculation of the dispersion relation of the wave and its physical characteristics), concluding with a brief explanation of the application of SPPs in optical sensors.

2.2.1 An Intuitive View of Surface Plasmon Polaritons

Propagation of electrons in metals is a central problem in Condensed Matter Physics, having suffered several advances in the XX century. While an accurate description of electron propagation can only be given by resorting to Quantum Mechanics (in particular the application of Bloch's theorem to the Schrödinger's equation) [124], the characteristics of SPPs are accurately described by the Drude-Lorentz classical model [125], due to the fact that the high carrier density in metals results in very short gaps in the energetic levels when comparing with thermal oscillations [126]. In this model the electronic motion is modelled as a driven dampened harmonic oscillator, meaning that the electrons are coupled to the metallic ions via an unspecified force modelled as a spring and driven by the electric field of the incident radiation. Nevertheless, the electrons within the last electronic layer can be considered as free to propagate in the metal (only keeping the Drude contribution of the Drude-Lorentz model), creating the possibility of excitation of plasma waves [127].

Consider now light incident on a metal - dielectric interface. Provided that the wavevector matches, the free electrons will be in resonance with the light's EM field oscillations, creating charge density waves called surface plasmons. The *polariton* term comes from the fact that light couples to the polarization within the media, and this effect severely influences the characteristics of the surface wave [127]. This is the basic principle behind surface plasmon resonance. In the next sections, the characteristics of this wave will be derived using a rigorous approach, casting light on the properties and dependence of this ESW.

2.2.2 Bound Modes at the Dielectric Metal Interface

Dispersion Relation of Surface Plasmon Polaritons

Consider the interface between a dielectric with permittivity ε_d and a metal with permittivity ε_m , as represented in Figure 2.3. Depending on the optical properties of the two media, this configuration may support a bound state.

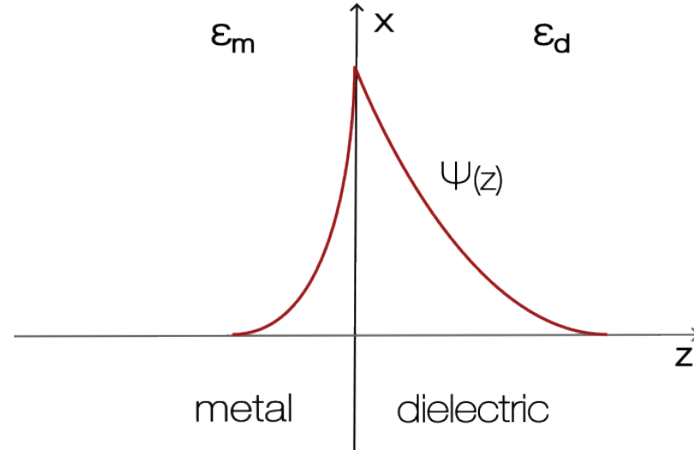


Figure 2.3: Interface between a metal and a dielectric, showing the field distribution in each domain.

As mentioned previously, ESWs decay exponentially away from the interface where they are generated. Given this exponential decay of the electric field in both regions of Figure 2.3, one can write the fields in each region as:

$$\begin{aligned}\Psi_1(z) &= \Psi(0)e^{-ik_{mz}z}, & z < 0 \\ \Psi_2(z) &= \Psi(0)e^{ik_{dz}z}, & z > 0\end{aligned}\tag{2.25}$$

where k_{mz} and k_{dz} are the perpendicular components of the wavevectors to the interface in both medium 1 and 2. Given the exponential decay of the fields, these components can be written as:

$$k_{mz} = i\kappa_m \quad \text{and} \quad k_{dz} = i\kappa_d, \quad \kappa_1, \kappa_2 \in \mathbb{R}\tag{2.26}$$

Derivation of the dispersion relation of SPP's can be easily done using the TMM formalism [121]. In this case, the fields in each side of the interface are related by a single interface matrix, yielding:

$$\begin{pmatrix} \Psi_2^+ \\ 0 \end{pmatrix} = M \begin{pmatrix} 0 \\ \Psi_1^- \end{pmatrix}\tag{2.27}$$

Using Equations 2.24, 2.11, 2.12 and 2.26, the dispersion relation for both TE and TM modes (considering non magnetic materials) is obtained:

$$\frac{\kappa_m}{\varepsilon_m} = -\frac{\kappa_d}{\varepsilon_d}, \quad p \text{ polarization} \quad (2.28)$$

$$\kappa_m = -\kappa_d, \quad s \text{ polarization}$$

In the case of the p polarization, Equation 2.28 implies that the sign of the permittivity of the materials on each side of the interface must change. On the other hand, in the case of the s polarization, no solution to Equation 2.28 is possible¹. Thus, excitation of this type of surface wave is only possible in the interface of a metal or heavily doped semiconductor [126] (which have negative permittivity) and a dielectric, and is called Surface Plasmon Polariton. Recasting equation 2.28 as function of the parallel component of the wavevector, using $k_x = \sqrt{k^2 - k_z^2}$, one obtains:

$$k_x = \frac{\omega}{c} \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}} \quad (2.29)$$

Equation 2.29 is the dispersion relation of SPPs, and introduces further restrictions on the existence this surface wave. Notice that by equation 2.28, $\varepsilon_m \varepsilon_d < 0$ (the permittivity changes sign at the interface). In order to make the parallel component of the wavevector a real quantity (to allow propagation along the interface), the denominator inside the root of equation 2.29 is also restricted and must be negative, giving the constraints:

$$\varepsilon_m \varepsilon_d < 0 \quad \text{and} \quad \varepsilon_d < -\varepsilon_m \quad (2.30)$$

The second condition in 2.30 can be writted as $\varepsilon_d < |\varepsilon_m|$, thus setting an additional condition between the optical properties of both media.

Incorporating the Drude model

Incorporating a model for the metal's permittivity allows further investigation on the properties of SPPs. Consider the lossy Drude model for metals [125], where the permittivity can be written as

$$\varepsilon_r = 1 - \frac{\omega_p^2}{\omega(\omega - i\gamma_p)} \quad (2.31)$$

¹Considering magnetic materials, Equation 2.28 for the s polarization includes the material's permeabilities and a solution is possible if the signal changes at the interface, which happens in some left-handed materials [128] and ferromagnetic resonances [129].

in which ω_p is the metal's plasma frequency² and γ_p is the damping constant, which parametrizes the losses of the metal. In order to illustrate the properties of real plasmonic configurations, four different metals were chosen, which are Silver, Gold, Copper and Aluminium. Their Drude parameters (expressed in wavelength units, where $\lambda_p = 2\pi/\omega_p$) are summarized in Table 2.1.

	Ag	Al	Au	Cu
λ_p (nm)	146.73	94.34	163.14	215.62
γ_p (nm)	25830	628.94	23393	41328

Table 2.1: Drude parameters for Silver, Gold Copper and Aluminium. Data taken from [130].

Figure 2.4 presents the SPP dispersion relation³ for a general metal-air interface using the Drude model (for lossy and lossless cases) and the dispersion relation for an SPP of real metals represented in Table 2.1.

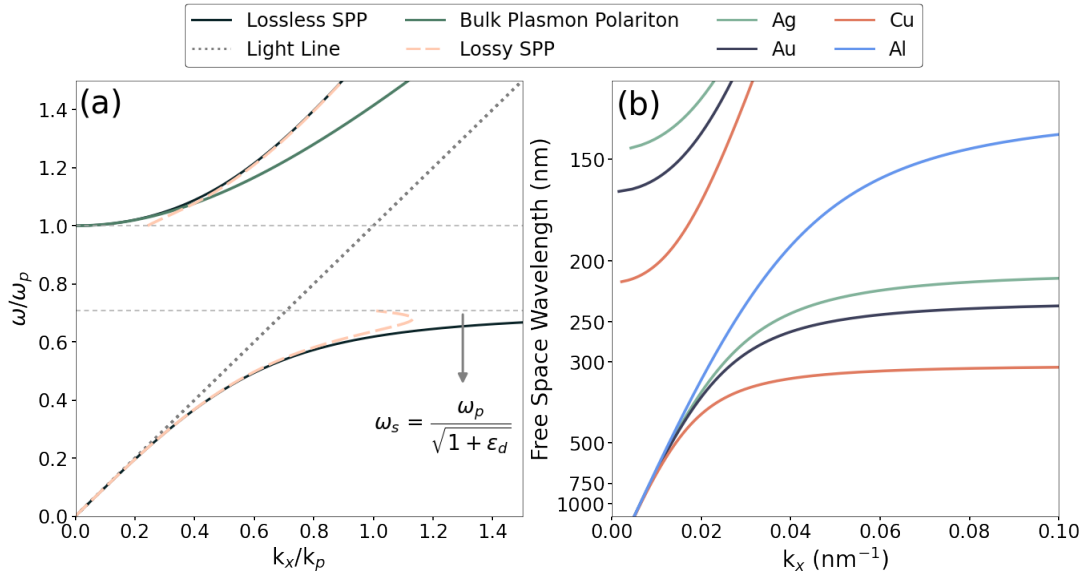


Figure 2.4: Dispersion relation of surface plasmon resonance for different metal-air ($\epsilon_d = 1$) interfaces. (a) General Drude metal for lossy ($\gamma_p = 0.1\omega_p$) and lossless ($\gamma_p = 0$) cases; (b) Ag, Au, Cu and Al dispersion relations. Notice that the four different metals tend to different values at high wavevectors.

Many interesting properties of SPPs can be explained from the analysis of Equation 2.29 and Figure 2.4. First of all, there exist two branches of the solution. The lower branch corresponds

²Plasma frequency is the frequency value in which the metal stops being highly reflective and becomes transparent (UV transparency) for higher frequencies, and is a characteristic of each material.

³It is common in the literature to represent the dispersion relation of an optical structure with the vertical axis units as angular frequency [122]. Nevertheless, in the optical sensors community, wavelength units are generally used. In order to keep the dispersion represented as frequency but in wavelength units, a transformation is made to the y axis, justifying the inversion seen in Figure 2.4 (b).

to the SPP, while the upper branch, which is not attainable by light excitation, consists of a Brewster Wave⁴ [127].

As can be seen in Figure 2.4 (a), at low ω and k values the SPP branch is light like, due to the proximity to the light line. This implies that at low k values the SPP dispersion relation becomes $k_x \approx \omega/c\sqrt{\epsilon_{r1}}$, which is the dispersion relation of light in a medium of permittivity ϵ_{r1} . On the other hand, when the permittivity of the metal and the dielectric have the same value but opposite signs, a pole is seen in Equation 2.29, corresponding to the asymptotic behaviour at high k values of Figure 2.4. This asymptotic value can be calculated from Equation 2.29 and corresponds to the cutoff frequency of the SPP, given by:

$$\omega_s = \frac{\omega_p}{\sqrt{\epsilon_{r1} + 1}} \quad (2.32)$$

Figure 2.4 (b) illustrates the dispersion relation of Silver, Gold, Copper and Aluminium SPPs. For low k values, the dispersion of all metals tends to the light line, in agreement with 2.4 (a). On the other hand, the asymptotic behaviour at high- k values is dependent on the plasma frequency of the metals, given by Equation 2.32, and as such is different for all metals. It can be seen that for the case of Copper no SPP mode is attainable at lower wavelengths than the near UV, while Gold, Silver and Aluminium support modes well into the UV range, which is dictated by the lower value of λ_p .

Two important consequences can be taken from the relation of the SPP dispersion and the light line. First of all, considering that the dispersion of SPPs is always below the light line, direct excitation of this mode is not possible due to mismatch of the wavevector (an incident wave will always have a parallel component of the wavevector below the SPP). This means that light coupling schemes have to be employed, meaning that a prism, grating or waveguide have to be used to provide the correct wavevector for SPP excitation [126]. On the other hand, given the fact that the parallel value of the wavevector is larger than the light propagation in the dielectric medium, the perpendicular component of the wavevector will be an imaginary number (which corresponds to an exponential decay in amplitude, Equation 2.22), meaning that the SPP cannot decay into a photon, making the SPP a non-radiative mode [127].

Also worth noting is the effect of losses caused by the imaginary part of the permittivity of the metal, which can be seen in Figure 2.4. In this case, $\gamma_p \neq 0$ is set in the Drude model, and represents a more realistic approach to modelling the optical properties of metals. It can be seen that the dispersion relation of SPP's is mainly affected in the high k region, where a bend is observed in the dispersion curve. The losses in plasmonic metals place a limit to the high values of wavevector that can propagate within metal layers, which would otherwise allow propagation of light with infinite value of wavevector in plasmonic modes.

⁴Not to be confused with a bulk plasmon, which is also plotted in Figure 2.4.

2.2.3 Physical Properties of Surface Plasmon Polaritons

From the dispersion relation for SPP's and assuming the Drude Model, the physical characteristics of this ESW can be derived. These characteristics, such as the SPP wavelength, propagation length and penetration depth, are the important factors to be considered in the design of optical devices which use SPP's. Barnes et al. [131, 132] provide an interesting discussion regarding the physical properties of SPPs and their application in optical devices and circuitry, discussing mostly size limitations as consequence of metal losses. In the case of optical sensors, the propagation length and penetration depths are of the upmost importance in device design due to direct correlation with the sensitivity and resolution of the sensor [133].

The physical properties of SPPs will be discussed for a particular set of metals (Silver, Gold, Copper and Aluminium), which are the most commonly used in plasmonics [126]. This allows a direct discussion by comparing values of these properties and their applications in devices. Solymar [127] presents a more generalized discussion using a general Drude Lorentz metal and calculating the properties of SPPs.

Wavelength

One of the most interesting properties of SPPs is the ability to confine light in regions with dimensions below the light's wavelength, a property called subwavelength confinement. This application of SPP's allows a high concentration of energy in very small regions, and has found applications in waveguides [8, 9] and nanoplasmonic lasers [134, 135]. Defining the SPP wavelength as $\lambda_{SPP} = 2\pi/k_x$ and using the SPP dispersion relation (Equation 2.29), one obtains:

$$\lambda_{SPP} = \lambda_0 \sqrt{\frac{\varepsilon_1 + \varepsilon_2}{\varepsilon_1 \varepsilon_2}} \quad (2.33)$$

Similarly to the dispersion relation, Equation 2.33 will display two different regimes. Figure 2.5 shows the relation between the free space and SPP wavelengths.

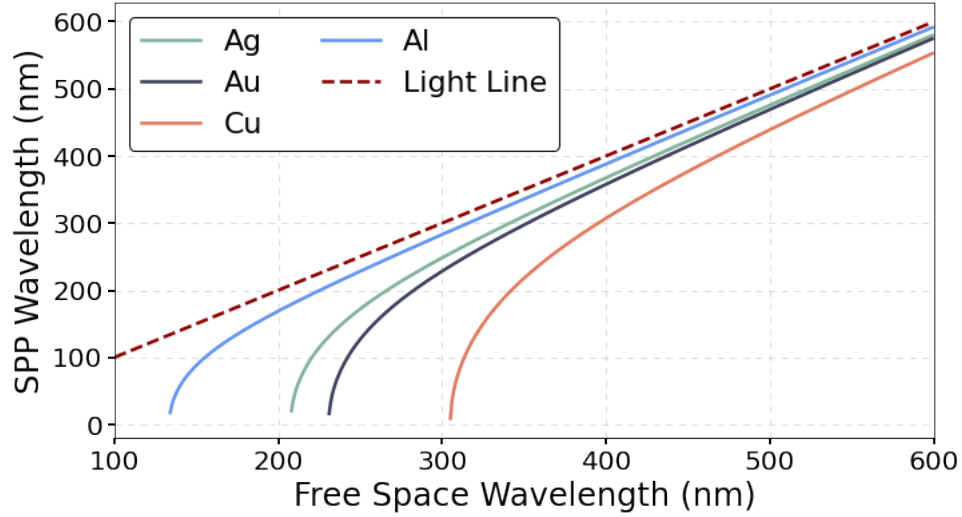


Figure 2.5: SPP wavelength as function of the free space wavelength. While at high values of wavelength the confinement of an SPP is only slightly inferior to that of free space light, at low wavelengths a critical behaviour is reached, where light becomes considerably subwavelength.

Figure 2.5 shows again the behaviour of an SPP at high values of wavelength (low k values) which is light like, and displays only slight difference from the free space wavelength of light. Nevertheless, at lower wavelengths (approaching the limit $\lambda_s = 2\pi c/\omega_s$), where the SPP becomes plasma like, subwavelength confinement of light is attainable. This property of SPPs is of extreme importance in plasmonic waveguides due to the ability of light confinement as scales much inferior than traditional waveguides [136].

Despite the higher losses, the confinement of light in the Cu plasmon is higher, due to the higher plasma wavelength, meaning that the SPP becomes plasma like at higher wavelengths, thus showing better confinement. Nevertheless, this higher value of λ_p also limits the minimum wavelength at high SPP excitation is possible, as seen in Figure 2.4. In the case of Ag and Au, significant differences are only present at low wavelengths, also due to the very close values of λ_p .

Propagation Length

It was seen previously that ESWs display exponential decay away from the interface where they are generated (Equation 2.22). Nevertheless, due to inherent losses associated with the material's properties (in this case, mostly with the metal), SPPs will also suffer exponential attenuation in the direction of propagation along the interface. Figure 2.6 illustrates the propagation of SPPs along a metal dielectric interface⁵ by plotting the magnitude of the transverse magnetic field H_y .

⁵Although the TMM is used in the work for the simulations, a COMSOL implementation of SPPs was used for the illustration in Figures 2.6 and 2.8. These simulations were set up by creating a simple metal-dielectric interface and incoming waves from one on the ports, with the software solving the field configurations in the defined mesh.

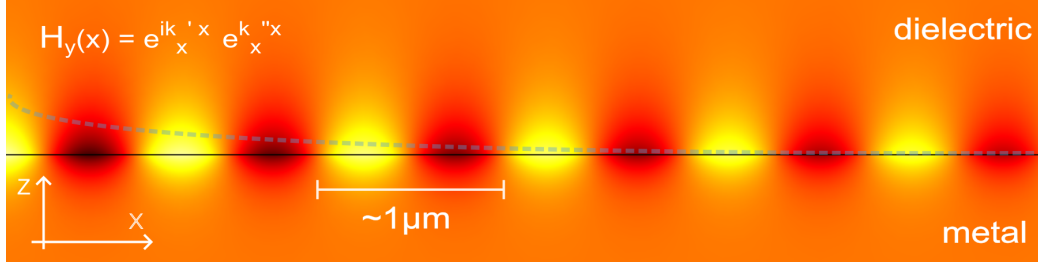


Figure 2.6: COMSOL simulation of the transverse magnetic field H_y of SPPs at a gold-air interface. Notice how the intensity of the field decays exponentially along the interface between the two materials.

Given that the decay along the interface is also exponential, as shown in Figure 2.6, the propagation length of an SPP is defined as the distance the wave travels before its intensity is reduced by a factor of $1/e$ [127]. This factor can be calculated directly from equation 2.29 by including losses in the material's permittivities. In this case, $k_x = k'_x + ik''_x$, and the plane wave contribution in the x direction assumes an exponential decay. In this case, the propagation length is defined as $L_{SPP} = 1/(2k''_x)$.

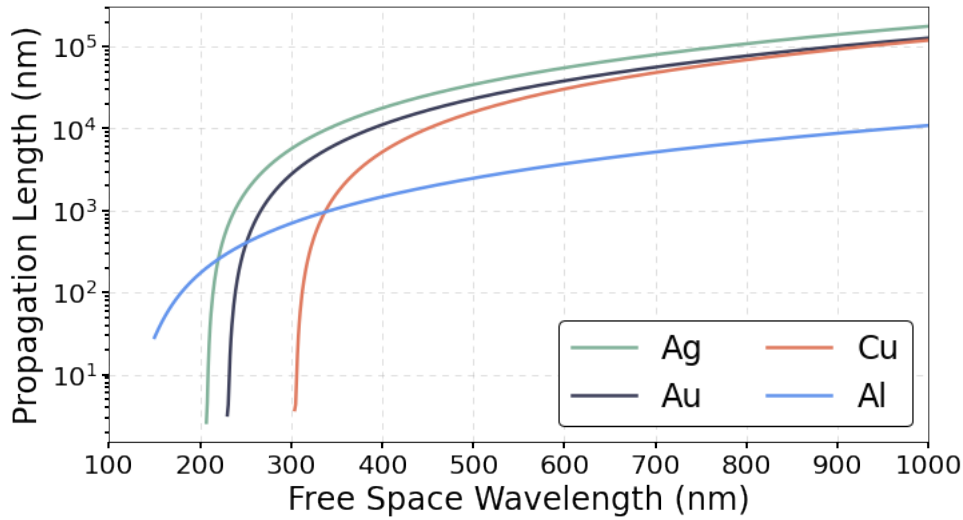


Figure 2.7: Propagation length of an SPP for various values of losses.

Figure 2.7 shows that for higher values of wavelength (where the SPP is light like) the propagation length is higher and several times the wavelength of the SPP, which is important for information manipulation [127] and for optical sensor applications [133]. The effect of losses induces a clear damping of the propagation length, which can be explained by higher scattering of the electrons in the interface, and the consequent decay of the SPP into heat. The response of the different metals seen in Figure 2.7 indicates a clear correlation of L_{SPP} with the imaginary part of the permittivity of each metal. Given that Aluminium is the material with highest losses (Table 2.1), the electrons in the SPP oscillations will decay faster into heat, leading to a lower propagation length. Notice also that in the case of the plasma like SPP (lower wavelengths), the

propagation length falls abruptly, which is due to a sharp increase of k_x'' in this region.

2.2.3.1 Penetration Depth

Another very important characteristic of ESWs is the penetration depth. As explained previously, the field of an ESW decays exponentially away from an interface, and the distance traveled by the wave until an attenuation of a factor of $1/e$ is called the penetration depth [127]. In the case of SPPs, the electromagnetic wave will decay exponentially away from the interface into both the metal and the dielectric, and both media will display different penetration depths, as illustrated in Figure 2.8.

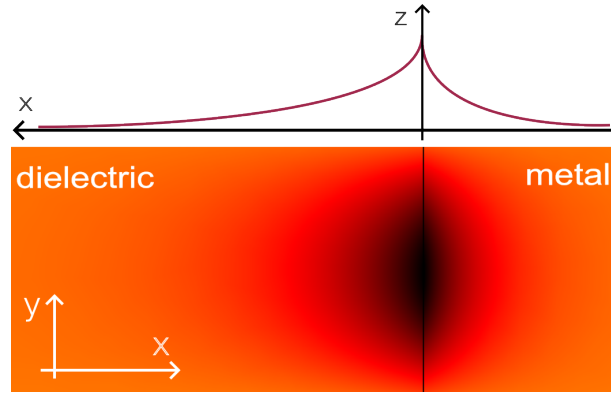


Figure 2.8: COMSOL simulation of the transverse magnetic field H_y of SPPs at a gold-air interface. Notice how the intensity of the field decays exponentially away from the interface between the two materials with two different decay constants.

Figure 2.8 illustrates the exponential decay of the transverse magnetic field away from the interface, showing the different decays to both sides. Given that the perpendicular component of the wavevector is an imaginary number (defined in Equation 2.26), the penetration depth within the metal can be defined as $\delta_m = 1/(2\kappa_m)$ and within the dielectric as $\delta_d = 1/(2\kappa_d)$. Using the dispersion of SPPs (Equation 2.29), the penetration depth can be determined as [133]:

$$\delta_d = \frac{\sqrt{\epsilon_m}}{k_x \epsilon_d}, \quad \delta_m = \frac{\delta_d \epsilon_d}{\epsilon_m} \quad (2.34)$$

The expressions in Equations 2.34 can be plotted as function of the wavelength for different materials.

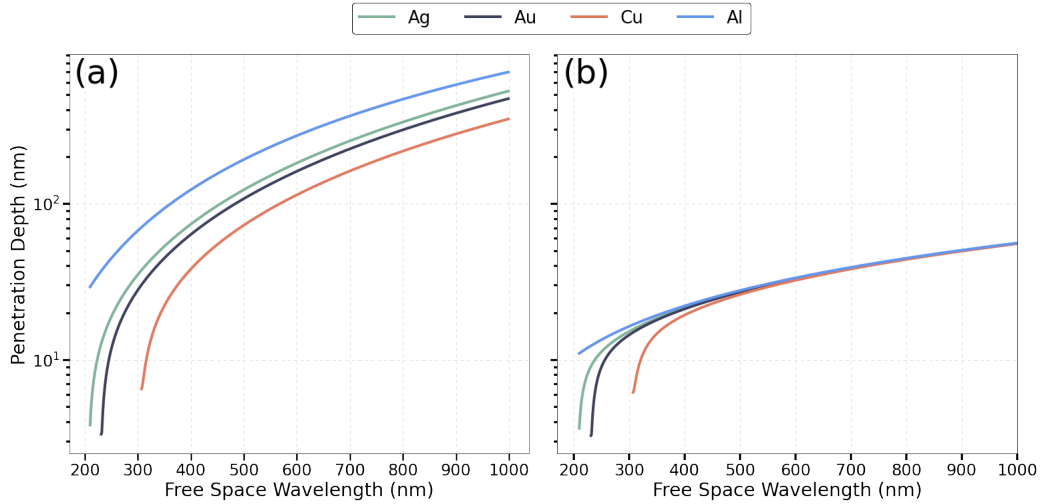


Figure 2.9: Penetration depth of Silver, Gold, Copper and Aluminium as a function of the wavelength: (a) Penetration depth into the dielectric; (b) Penetration depth into the metal.

It can be seen for all metals represented in Figure 2.9 (a) that the penetration depth into the dielectric increases considerably with increasing wavelength, and also shows an abrupt decrease at low wavelengths. Solymar [127] provides an explanation of this phenomenon by remarking that metals are better conductors at longer wavelengths (away from the plasma frequency, where the free electrons can keep up with the light oscillation), leading to significantly less damping of the SPP. This characteristic of the SPP is of extreme importance to application in optical sensors due to the fact that the sensitivity of the device is highly dependent on the power that propagates in the dielectric. Of the plasmonic metals considered, Aluminium shows the highest penetration depth into the dielectric, followed by Silver and Gold. This ordering can be explained by Equation 2.34, where it can be seen a direct dependence with the square root of ϵ_m . Given that Aluminium has the lowest λ_p , it will also have the highest ϵ_m (in absolute value), thus explaining the higher penetration depth. On the other hand, all metals seem to display similar penetration depths into the metal except at low wavelengths, near their value of λ_p . This field penetration (which is much less than into the dielectric) is of extreme importance in the generation of SPP modes on both interfaces of the metal film, which will be explored in section 2.4. In order to generate these modes, the field penetration must allow the coupling of the fields on both interfaces, and as such the metal film must be considerably thin.

2.2.4 Surface Plasmon Resonance Based Sensors

Given the physical characteristics of SPPs, we can now approach the application of this ESW in optical sensors. As mentioned previously, a large fraction of the power associated with the SPP propagates on the dielectric medium, and as such the ESW will be extremely sensitive to variations of the optical properties of this dielectric layer. SPR based sensors take advantage of this high sensitivity to monitor both variations of refractive index of the dielectric layer or for molecule detection using functionalized surfaces that bind to a specific molecule.

In this work, the excitation of SPPs using a prism coupling technique is considered, although grating excitation is also a relevant method [126]. In SPP sensors, the coupling conditions of the mode vary with the variation of the external RI, meaning a shift will be detected by the experimental setup. This shift provides four different methods of interrogating plasmonic structures, which are the spectral, angular, intensity and phase interrogation. Only the spectral interrogation mode, which detects a wavelength shift of the SPP (and as such requires a white light source and a spectrometer), is considered here. Homola [48] provides an excellent analysis of the different interrogation methods of SPPs.

2.2.4.1 Prism Excitation of Surface Plasmons

Prism excitation using the Kretschmann configuration [20, 48] in the spectral mode (fixed angle and broadband illumination) is considered, which is illustrated in Figure 2.10.

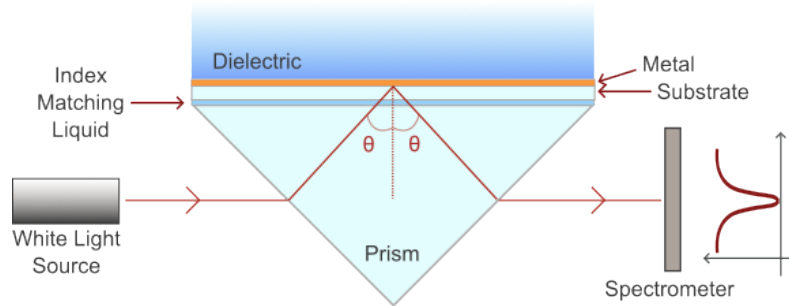


Figure 2.10: SPP Excitation using the Kretschmann configuration. A prism of higher RI than the external dielectric is used to match the SPP wavevector, which does not allow direct excitation.

In Figure 2.10, white light is coupled to the prism and suffers Attenuated Total Reflection (ATR) in the interface between the prism and the film at an angle θ , allowing the wavevector to match the SPP resonance, which is not possible under direct incidence, as seen previously. The light is collected with a spectrometer and a peak in the reflectivity is seen, which indicates the presence of the SPP. The basic principle behind SPP sensors can be easily understood from the dispersion relation. The resonance peak is present in the wavelength where the SPP dispersion and the prism dispersion match. By changing the properties of the dielectric (whether by variations in the refractive index or by slight perturbations due to the presence of molecules close to the interface), the coupling conditions will change because a variation of the optical properties of the dielectric will be seen. In the case of RI variations, the value of ϵ_d will change, leading to a modification of the dispersion relation (Equation 2.29). Figure 2.11 illustrates this process.

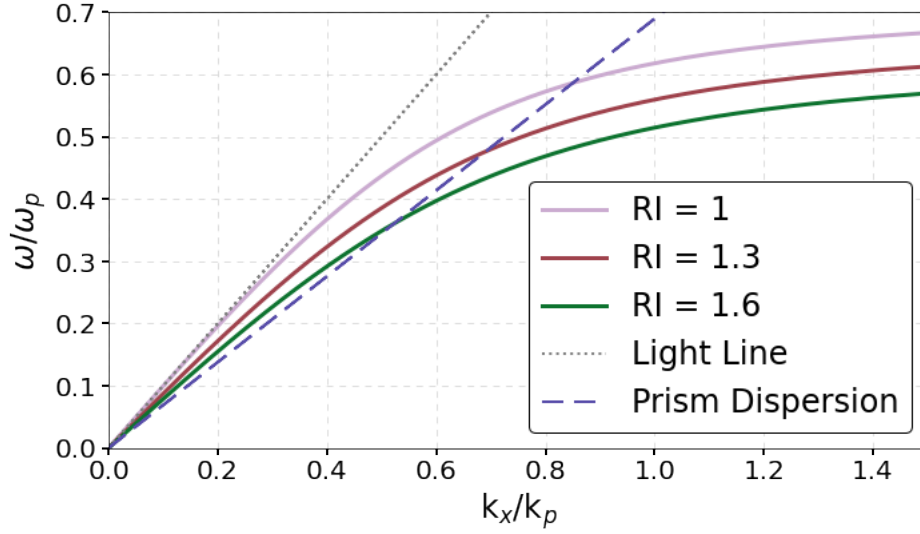


Figure 2.11: SPP based sensor principle seen in the dispersion relation perspective. A variation of the RI of the external dielectric leads to a change in the coupling conditions of the mode, creating a detectable shift in the resonance peak.

Figure 2.11 shows how a variation of the RI of the dielectric leads to a variation of the peak wavelength (vertical axis) by changing the conditions of the mode, which can easily be understood by variations of ε_d in Equation 2.29. While Figure 2.11 provides the basic physical picture behind an SPP sensor, in practice the presence of a prism will induce slight variations to the mode. In this case, the parallel component of the wavevector k_x^{SPP} can be defined as [48]:

$$k_x^{SPP} = k_x^{SPP_0} + \Delta k_x = \frac{2\pi}{\lambda} \sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}} + \Delta k_x \quad (2.35)$$

where $k_x^{SPP_0}$ is the dispersion relation of the SPP in the metal dielectric configuration (Equation 2.29) and Δk_x is a correction induced by the effect of the prism due to the finite thickness of the metal. In the case of prism excitation, the SPR resonance will be observed in a spectral position where the propagation constants of the SPP and the prism match, that is $k_x^{SPP} = 2\pi/\lambda n_p \sin \theta$, where n_p is the prism's RI and θ is the incidence angle.

An important quantity in guided modes (ESWs or conventional guided modes) is the effective index, which is defined as $n_{ef} = k_x \lambda / (2\pi)$. In the case of the SPR excitation under the Kretschmann configuration, the effective index is given by:

$$n_{ef} = n_p \sin \theta = \text{Re} \left\{ \sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}} \right\} + \Delta n_{ef}^{SP} \quad (2.36)$$

where $\Delta n_{ef}^{SP} = \text{Re}\{\Delta \beta \lambda / (2\pi)\}$. It can be seen that the experimental conditions also affect the SPR position (besides the structure materials) are the incidence angle and the prism refractive index. For an almost dispersionless prism (at least in the wavelength range used), the SPR

position is mainly dictated by θ . Figure 2.12 illustrates this dependence on the incident angle.

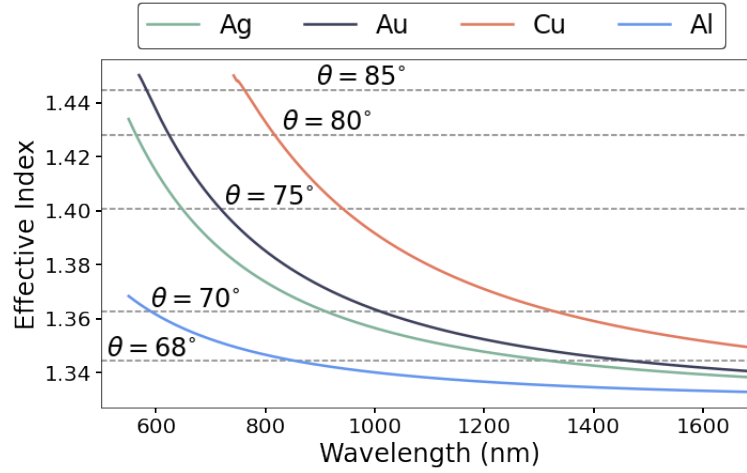


Figure 2.12: Spectral dependence of the effective index of SPR for different plasmonic metals, considering an SiO_2 prism. Dashed lines mark different incidence angles on the prism surface, showing how the spectral position is dictated by θ .

It can be seen in Figure 2.12 that the spectral position of the SPP can change drastically depending on the incidence angle. As expected from the definition of effective index, the lower the plasma wavelength is, the lower the effective index at the same wavelength is. As will be seen, the incidence angle will also have an effect on sensitivity and linewidth of the resonance, which are also important metrics for the SPR sensor.

2.2.4.2 Sensitivity of Surface Plasmon Based Sensors

One of the most important features associated with optical sensors is the sensitivity S , defined as the ratio between the change in the sensor output Y (whether it's peak wavelength, angle, intensity or phase) to the change in the measurand X [48]:

$$S = \frac{\partial Y}{\partial X} \quad (2.37)$$

Generally speaking, SPR based sensors can be used for two different purposes [133, 48]. If an SPR sensor measures variations in the refractive index of the external dielectric n , the refractometric sensitivity S_{RI} is used:

$$S_{RI} = \frac{\partial Y}{\partial n} \quad (2.38)$$

Another common use for SPR sensors is affinity sensing, in which the surface of the device is functionalized in order to bind to a specific molecule for detection. This binding event will

slightly change the coupling conditions of the SPP, resulting in a detectable change in the sensor's output. In this case the sensitivity S_c to the concentration c of a specific analyte is defined as:

$$S_c = \frac{\partial Y}{\partial c} \quad (2.39)$$

Consider the refractometric sensitivity of an SPR sensor, detected by a change in the peak resonance wavelength λ_r . Using the chain rule of differentiation, one can write:

$$S_{RI} = \frac{\partial \lambda_r}{\partial n} = \frac{\partial \lambda_r}{\partial n_{ef}} \frac{\partial n_{ef}}{\partial n} \quad (2.40)$$

In Equation 2.40, the first derivative in the last term is referred to as the instrumental contribution [48] and is dependent of the experimental method of excitation of the SPR (prism or grating). The second term in the last equality is the sensitivity of the effective index of a surface plasmon to variations of the external refractive index.

The instrumental contribution can be determined by differentiating the coupling conditions of the prism (Equation 2.36) and applying the inverse function rule of derivation, yielding:

$$\frac{\partial \lambda_r}{\partial n_{ef}} = \frac{1}{\frac{dn_p}{d\lambda} \frac{n_{ef}}{n} - \frac{dn_{ef}}{d\lambda}} \quad (2.41)$$

From Equation 2.41 it can be seen that the instrumental contribution depends on the chromatic dispersion of the prism and the dispersion of the effective index of an SPP. Given that most glasses used in prisms are only slightly dispersive, the main contribution comes from the dispersion of n_{ef} .

The sensitivity of the effective index of an SPP has been calculated using first order perturbation theory [133, 48], considering a small perturbation to the external dielectric's RI, and can be written as:

$$\frac{\partial n_{ef}}{\partial n} = \frac{n_{ef}^3}{n^3} \quad (2.42)$$

The spectral sensitivity can now be calculated using Equation 2.40, yielding [48]:

$$S_\lambda = \frac{\varepsilon'_m{}^2}{-\frac{n^3}{2} \frac{d\varepsilon'_m}{d\lambda} + \varepsilon'_m \left(n^2 + \varepsilon'_m \frac{n}{n_p} \frac{dn_p}{d\lambda} \right)} \quad (2.43)$$

Equation 2.43 reveals some important features of optical sensors. Firstly, the sensitivity increases with the decrease of permittivity of the metal (which is negative). On the other hand, the dispersive behaviour of the metal and prism permittivity lead to a decrease in sensitivity, meaning a low dispersion prism should be employed. Figure 2.13 illustrates the typical values for the different metals considered.

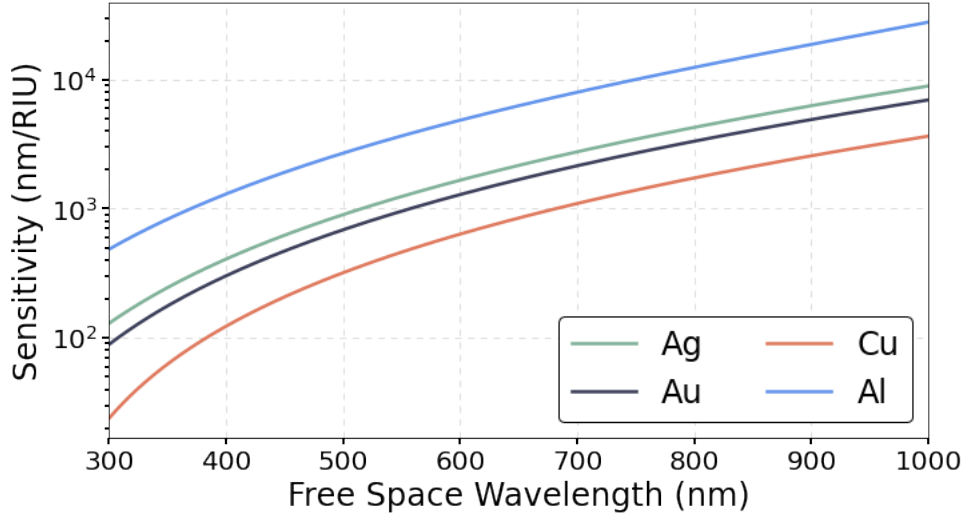


Figure 2.13: SPR sensitivity to RI variations for different metals near RI = 1.333 (water).

From Figure 2.13 it can be seen that a direct correlation of the plasma wavelength with the sensitivity can be seen, in particular that the lower the plasma wavelength, the higher the sensitivity, explaining why Al is the most sensitive metal. This can be explained using Equation 2.43, where it can be seen that the higher the absolute value of ϵ'_m (which is directly related to λ_p), the higher the sensitivity. Combining Figures 2.12 and 2.13 it can be seen that a correct choice of angle can improve the sensitivity of the device drastically.

Comparison of performance between different sensors (whether of different plasmonic configurations or different ESWs) requires the use of a universal metric, applicable to all. In most sensor applications this comparison can be done using the Figure of Merit (FoM), defined as [137]:

$$FoM = \frac{S_\lambda}{FWHM} \quad (2.44)$$

The FoM consists of the ratio between the sensitivity and the full width at half maximum (FWHM) of the resonance, as seen in Equation 2.44. A sensor with a better performance will have a higher FoM, which can happen due to an increase in the sensitivity or a decrease in the FWHM. The lower the FWHM, the sharper the resonance will be and consequently there will be less uncertainty on the determination of the peak wavelength, justifying the higher FoM.

Raether [138] tackled the problem of modelling the FWHM associated with an SPR band under the assumption of a lorentzian approximation to the curve and that radiative and absorptive losses are equal, which result in the optimal coupling conditions. This implies that the metal has the optimal thickness for SPR excitation, which was determined to be around 50nm for Gold and Silver [48]. Under these assumptions, the FWHM is given by:

$$FWHM = \frac{4\gamma}{\left| \frac{dn_p}{d\lambda} \sin \theta - \frac{dn_{ef}}{d\lambda} \right|} \quad (2.45)$$

where $\gamma = \text{Im}\{k_x^{SP_0}\}\lambda/(2\pi)$. The variation of the the FWHM under the optimal coupling conditions can be studied as a function of wavelength, and using Equation 2.43, the FoM can be analytically calculated.

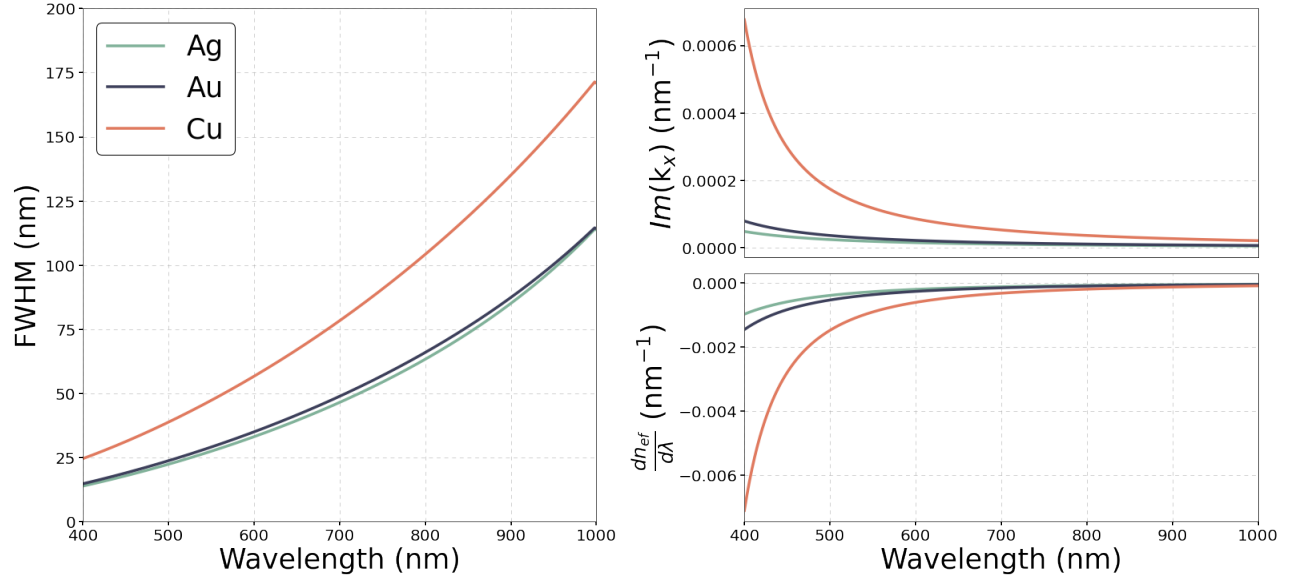


Figure 2.14: Characteristics of SPR sensors with different metals: (a) FWHM; (b) Imaginary part of k_x ; (c) Derivative of the effective index with the wavelength.

Figure 2.14 (a) displays the FWHM for the considered metals. It is interesting to observe that with this model the Silver SPP is the sharper resonance, which is confirmed in Figures (b) and (c) in which the Silver plasmon is shown to display the smallest imaginary part of the wavevector and largest chromatic dispersion of the effective index, all important parameters in the SPP sensitivity (as seen in Equation 2.43). The case of Aluminium is not represented in Figure 2.14 due to the fact that the FWHM calculations give a prediction of an order of magnitude superior to the other metals, indicating that the approximation made may not apply to this high loss material.

2.3 Bloch Surface Waves

The second type of surface wave to be studied in this work is called Bloch Surface Wave (BSW), which is generated at the interface between a photonic crystal (PhC) and a dielectric medium. A brief introduction to photonic crystals and BSWs in 1D systems is given here, providing both a mathematical (based on the TMM formalism) and an intuitive picture of the physics behind BSW's. Along with the description of this ESW, the application to optical sensors is studied, where some novel theoretical results are presented.

matrix (Equation 2.13). By employing Equation 2.24, the dispersion relation of the modes associated with the unit cell structure can be made numerically for both polarizations. The dispersion relation of the unit cell is presented in Figure 2.16.

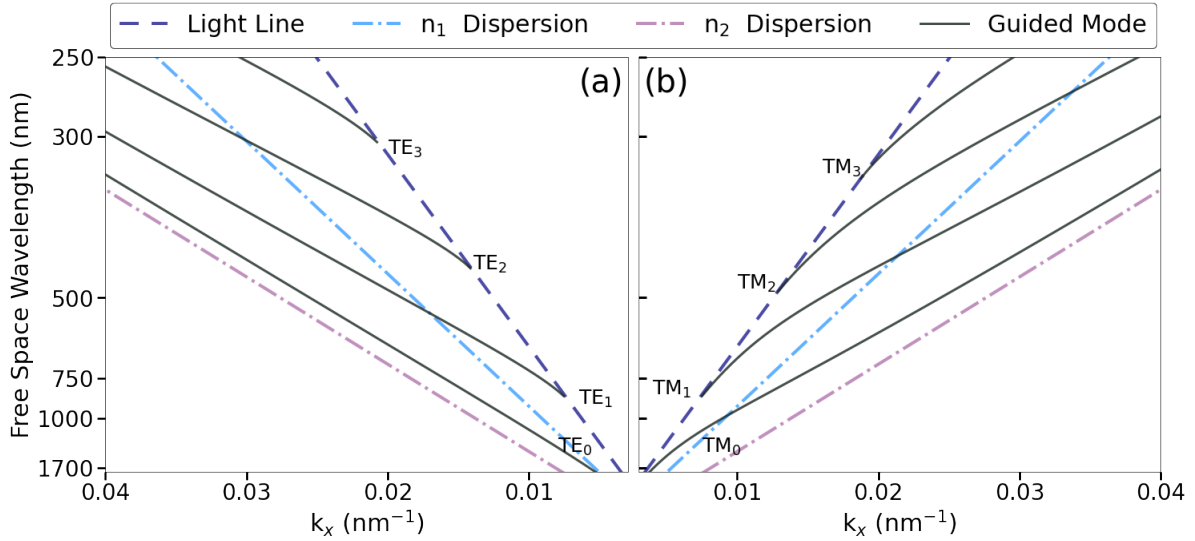


Figure 2.16: Dispersion relation of a unit cell of a PhC, with $n_0 = 1$, $n_1 = 1.45$, $n_2 = 2.20$, $d_1 = 100\text{nm}$ and $d_2 = 200\text{nm}$. (a) s polarization; (b) p polarization.

Figure 2.16 shows the dispersion relation of the unit cell structure for both polarizations. It can be seen that multiple modes exist, corresponding to typical TE and TM modes similar to those seen in a slab waveguide. These modes correspond to solutions to Maxwell's Equations within the given geometry, and will display electric and magnetic field configurations according to their frequency and wavevector values. The modes are generally labeled according to the number of nodes they display (for example, TE_0 , TE_1 , ...), as is typical of all dielectric waveguides [139].

The considered unit cell structure behaves very similarly to a typical waveguide, displaying both TE and TM modes which are mostly confined to the waveguiding layer. The low RI layers create a shift in the effective index of the modes, creating a small deviation from the single slab waveguide. Nevertheless, as will be seen, the thickness and RI of this low RI layer will be of extreme importance in the characteristics of a PhC, in particular in the width of the allowed bands of light propagation.

2.3.2 Photonic Crystals: Infinite Case

Having analysed the case of a single unit cell, the problem of the superposition of N unit cells is now tackled, forming an infinite PhC. The illustration and RI profile of such a structure is presented in Figure 2.17.

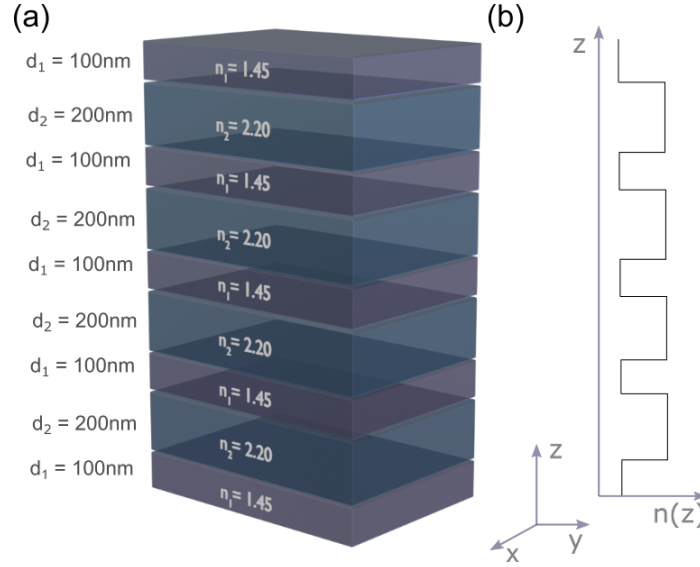


Figure 2.17: Infinite PhC composed n unit cells: a) 3D illustration, b) RI profile.

The problem of modelling such a structure can be approached from different perspectives, such as using Bloch's Theorem [55], Chebyshev's Theorem [122, 121] or other techniques such as equivalent layers and Herpin index [62, 77]. In this work Bloch's Theorem will be employed, but providing a physical picture by explaining how the properties of PhC stem from the unit cell waveguide studied previously.

The RI profile of Figure 2.17 can be written as

$$n(z) = \begin{cases} n_1, & m\Lambda < z < m\Lambda + d_1 \\ n_2, & m\Lambda + d_1 < z < (m+1)\Lambda \end{cases} \quad (2.47)$$

where $m \in \mathbb{N}$. It can be seen that over a unit cell length $\Lambda = d_1 + d_2$ the RI is periodic, meaning that $n(z + \Lambda) = n(z)$.

Considering the wave equation obtained in Equation 2.4 and given that the fields are time harmonic, using the monochromatic plane waves of Equation 2.5 in the time derivative, one obtains:

$$(\nabla^2 - \mu_0 \varepsilon \omega^2) \vec{E} = 0 \quad (2.48)$$

Due to the periodic modulation of the RI shown in Equation 2.47, the second term in the brackets of Equation 2.48 is a periodic function. Analysis of this equation reveals that it is formally identical to the time independent Schrödinger Equation of an electron in a crystal [124], and in a more general approach it is one of the many applications of Hill's Equation [140]. Given the formal similarity with Schrödinger's Equation, Bloch's Theorem is also applicable in this photonic structure, and states that the field inside the PhC is given by:

$$\Psi(z) = \Psi_K(z)e^{iKz} \quad (2.49)$$

where $\Psi_K(z)$ is a function with the same periodicity as the lattice and K is a constant called the Bloch number, of which $\Psi_K(z)$ also depends.

Analysis of such a system is possible by employing the Transfer Matrix formalism along with Bloch's Theorem. Given the field configuration given by Equation 2.49, one can write the transfer matrix of one unit cell as:

$$\begin{pmatrix} \Psi_n^+ \\ \Psi_n^- \end{pmatrix} = \mathbf{M} \begin{pmatrix} \Psi_{n-1}^+ \\ \Psi_{n-1}^- \end{pmatrix} = e^{iK\Lambda} \begin{pmatrix} \Psi_{n-1}^+ \\ \Psi_{n-1}^- \end{pmatrix} \quad (2.50)$$

Equation 2.50 implies that $e^{iK\Lambda}$ is an eigenvalue of the transfer matrix $\mathbf{M}$, and can be calculated by

$$e^{iK\Lambda} = \frac{1}{2}(A + D) \pm \sqrt{\left[\frac{1}{2}(A + D)\right]^2 - 1} \quad (2.51)$$

where A and D are the diagonal entries of $\mathbf{M}$, which can be obtained from Equations 2.12 and 2.11. From Equation 2.51, the dispersion relation of Bloch Waves, which are waves that propagate inside a PhC, can be determined:

$$K(k_x, \omega) = \frac{1}{\Lambda} \arccos \frac{1}{2}(A + D) \quad (2.52)$$

The eigenvectors corresponding to the eigenvalues $e^{iK\Lambda}$ are:

$$\begin{pmatrix} \Psi_0^+ \\ \Psi_0^- \end{pmatrix} = \begin{pmatrix} B \\ e^{iK\Lambda} - A \end{pmatrix} \quad (2.53)$$

Equation 2.52 is central to the understanding of the behaviour of PhCs and the generation of allowed and forbidden bands of light propagation. This equation presents two different regimes [122]: first where $|1/2(A + D)| < 1$, in which $K \in \mathbb{R}$ and corresponds to a propagating Bloch wave, as seen in Equation 2.49; secondly where $|1/2(A + D)| > 1$, and $K = m\pi/\Lambda + iK_i$, where m is an integer and $K \in \mathbb{C}$, where K_i is the imaginary part. These second type of solutions are evanescent in the PhC (as indicated by Equation 2.49), and as such do not propagate in the structure. These two regimes form the basis of allowed and forbidden bands of the PhC: in allowed bands K will be a real number, while in forbidden bands K will be a complex number. Figure 2.18 shows the dispersion diagram of the s polarization of the infinite PhC structure of Figure 2.17, as well as the Bloch number K along the dispersion of n_1 , calculated using Equation 2.52.

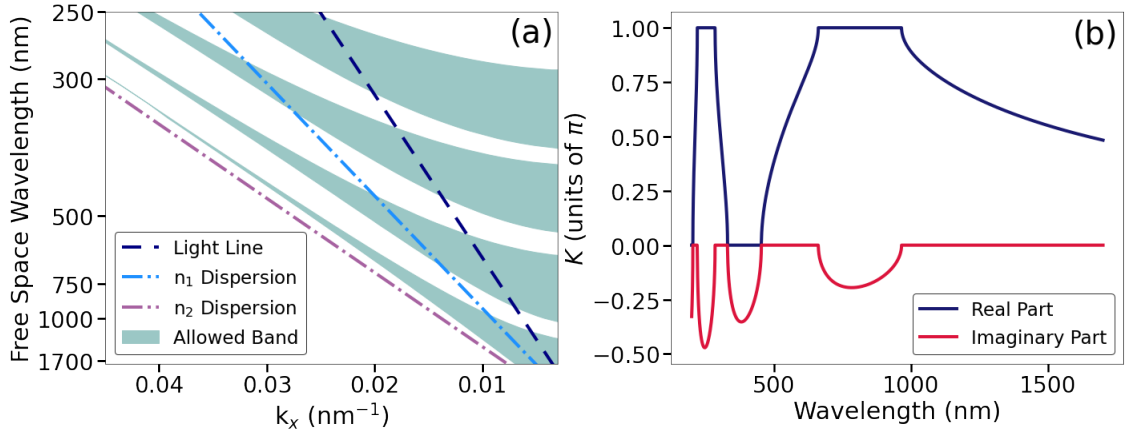


Figure 2.18: Infinite PhC structure: a) Dispersion relation for the s polarization; b) Bloch Wave number as a function of the wavelength along the dispersion of n_1 .

Figure 2.18 confirms the analysis made previously, where it can be seen that for allowed bands $K_i = 0$ and for forbidden bands $K = m\pi/\Lambda + iK_i$. In the forbidden bands, light is reflected off the PhC structure, which is a property used in the design of filter and coatings [77].

The origin of allowed bands can be traced back to the modes of the single unit cell. Consider a system of four stacked unit cells equal to that presented in Figure 2.15. The dispersion relation of this structure is shown in Figure 2.19.

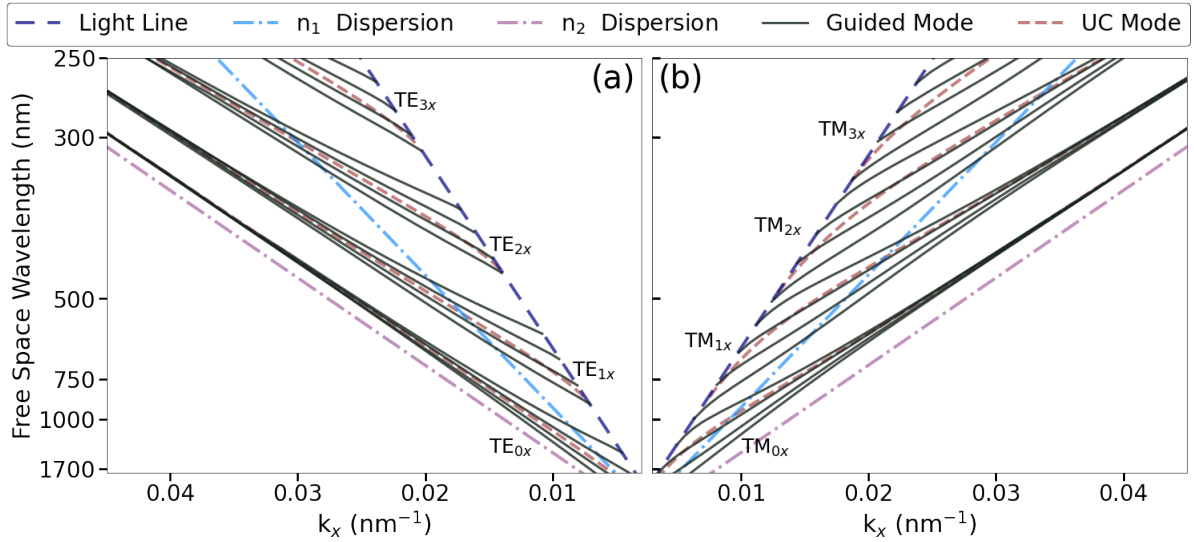


Figure 2.19: Dispersion relation for a PhC composed of 4 unit cells with $n_0 = 1$, $n_1 = 1.45$, $n_2 = 2.20$, $d_1 = 100\text{nm}$ and $d_2 = 200\text{nm}$: a) p polarization, b) s polarization.

Figure 2.19 shows how the modes of the PhC composed of four unit cells relate to the original modes of the single unit cell. At high values of the wavevector, the fields are more confined inside the high RI layers, and modes within different unit cells do not interact with each other. Nevertheless, at low k values, the modes of different unit cells interact with each other, lifting

their degeneracy and giving rise to 4 new non-degenerate modes. Considering again the infinite PhC, it can be seen that infinite modes will be generated in this degeneracy lifting process, thus completely filling a band of allowed states of the structure. These bands, also represented in Figure 2.19, are the allowed bands of light propagation.

Given that the PhC modes originate from the original modes of the single unit cell, Yeh [122] proposed maintaining the conventional mode nomenclature but adding another number to the subscript to separate the new, non degenerate modes. It can be shown that for a PhC with N unit cells, N modes will emerge from the original one. For example, a TE_0 mode will originate N new modes, being labelled TE_{00} , TE_{01} , $\dots$, TE_{0N} . Figure 2.20 illustrates the electric field profiles of TE modes excited by a prism coupling scheme (guided mode resonance - GMR).

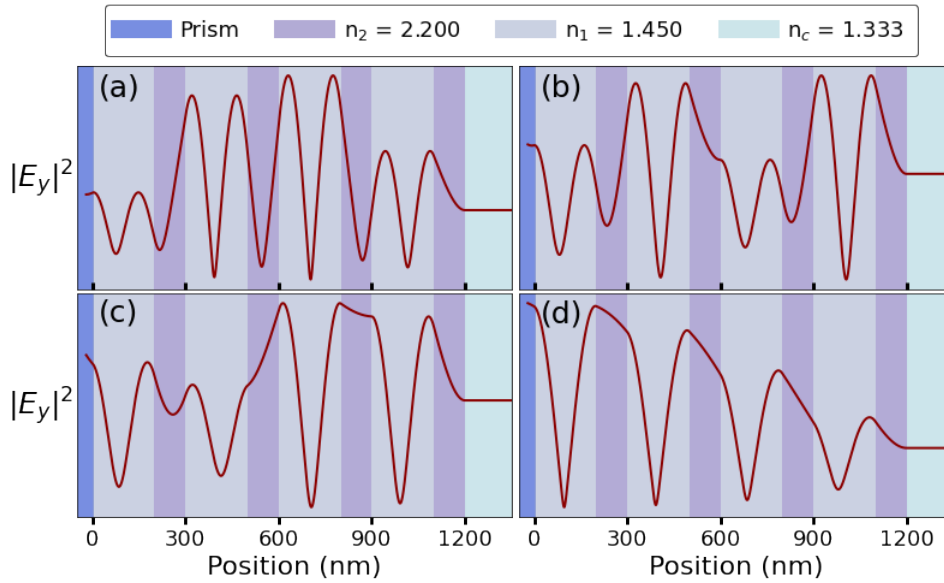


Figure 2.20: Magnetic field profiles of the TE_{0x} modes inside a 4 unit cell PhC: (a) TE_{00} , (b) TE_{01} , (c) TE_{02} , (d) TE_{03}

Figure 2.20 shows the new modes generated from the original TE_0 mode of the single unit cell. Notice how the modes with lower index (which correspond to lower frequencies) have the field mostly in the high RI layers, and with progressive increase of mode number the field starts to shift to the low RI layers. This is an analog of the particle in a periodic potential barrier in Quantum Mechanics: only higher energy solutions have their wavefunctions in low potential areas [141].

2.3.3 Photonic Crystals: Truncated Case

Having explained the basic principle behind the formation of PhCs, a more realistic structure is now considered, with a finite number of unit cells and a truncated top layer composed of the high RI material with thickness $d_s = 140\text{nm}$. An external cladding of RI n_0 is in contact with the cap layer of the PhC. This configuration is illustrated in Figure 2.21 for the case of 4 unit cells.

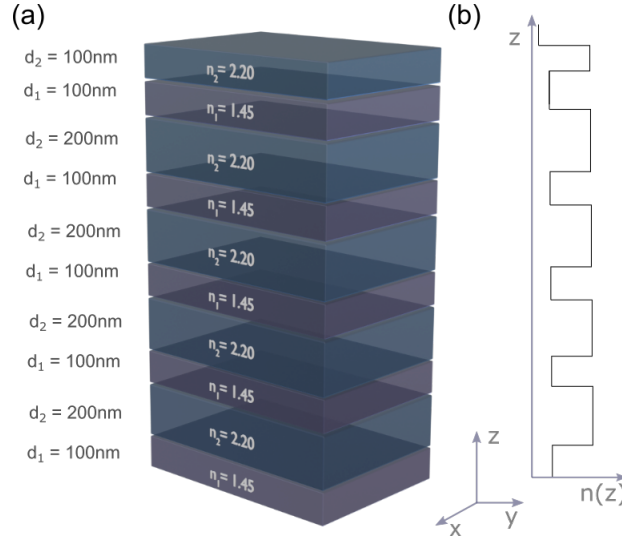


Figure 2.21: Illustration of a PhC composed 4 unit cells with $n_1 = 1.45$, $n_2 = 2.2$, $d_1 = 100\text{nm}$ and $d_2 = 200\text{nm}$. The cap layer of RI n_2 has thickness $d_s = 140\text{nm}$, creating a symmetry breaking of the RI profile: (a) PhC Structure; (b) Refractive Index profile.

Addition of a high RI truncated layer in a PhC may lead to the formation of an ESW as result of the symmetry breaking of the periodic modulation of the RI. Inside each layer the solution to Maxwell's Equations will be a sum of a forward and a backwards propagating wave. This wave can be written as:

$$\Psi(z) = a_s e^{ik_{2z}z} + b_s e^{-ik_{2z}z} \quad (2.54)$$

where a_s and b_s are the forward and backward propagating plane wave amplitudes. In the truncated layer, a different phase will be added to the wave, and the plane wave coefficients can be written as

$$\begin{pmatrix} a_s \\ b_s \end{pmatrix} = P_2 \begin{pmatrix} B \\ e^{iKz} - A \end{pmatrix} = \frac{1}{2} \begin{pmatrix} B e^{-2ik_z d_s} \\ e^{iK\Lambda} - A \end{pmatrix} \quad (2.55)$$

which implies that the last layer simply adds a phase difference to the wave, which is incorporated in the eigenvector of Equation 2.53. Outside of the PhC, the field decays exponentially and is given by:

$$\Psi(z) = \alpha e^{q_0 z} \quad (2.56)$$

where $q_0 = \sqrt{k_x^2 - k_{z0}^2}$. In this case, by matching the fields and the derivatives in Equations 2.54 and 2.56 at the interface of the PhC with the external cladding, one obtains:

$$q_0 = -ik_1 \frac{e^{iK\Lambda} - A - Be^{-2ik_z d_s}}{e^{iK\Lambda} - A + Be^{-2ik_z d_s}} \quad (2.57)$$

The dispersion relation in Equation 2.57 needs to be solved numerically for both polarizations. Figure 2.22 demonstrates the dispersion relation of a BSW along with the bands of the PhC.

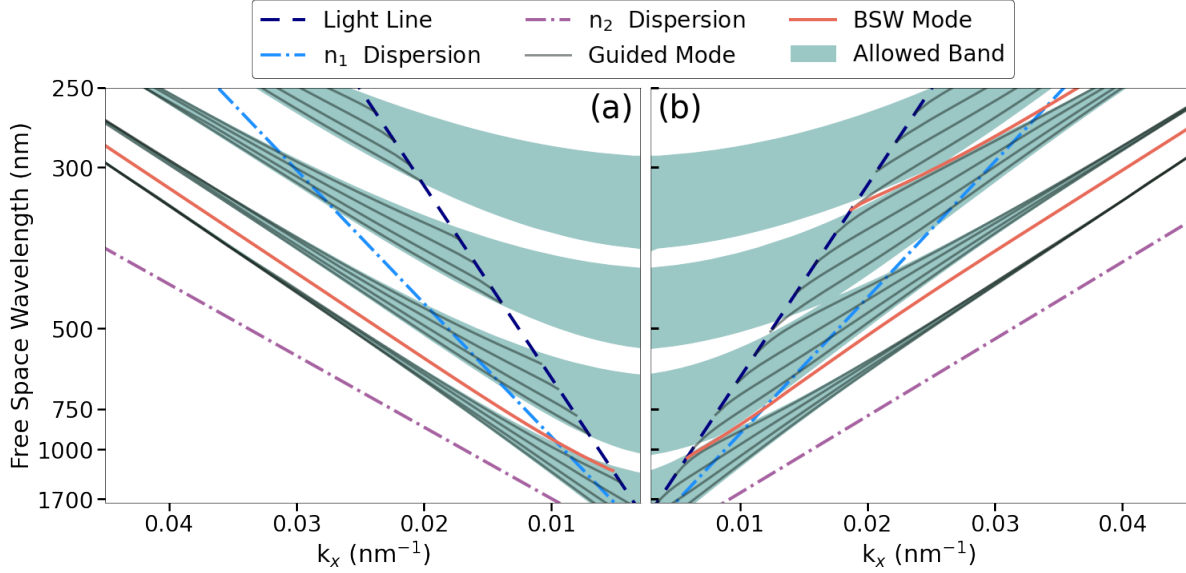


Figure 2.22: Dispersion relation of a semi infinite PhC with a truncated layer, with $n_0 = 1$, $n_1 = 1.45$, $n_2 = 2.2$, $d_1 = 100\text{nm}$, $d_2 = 200\text{nm}$ and $d_s = 140\text{nm}$: a) s polarization, b) p polarization.

In Figure 2.22 it is possible to observe the same band structure as in 2.19, and the BSW modes which propagate in the forbidden bands of the PhC. Notice how, similarly to SPPs, the BSW dispersion lies below the light line, meaning that direct excitation of this mode is not possible. Similarly to SPPs, a coupling scheme using a prism, grating or waveguide is needed in order to excite BSWs.

Yeh argues about the existence of BSWs as a consequence of both the symmetry breaking of the PhC at the surface and the interaction between the different waveguides [55]. In a truncated PhC, all the waveguides (the high RI layers) are identical with the exception of the one in the surface. The modes supported by these waveguides at infinite separation are degenerate, but when the fields interact with each other this degeneracy lifts, creating the allowed band of propagation. This band is occupied by the N many modes that originate from the degenerate state, and as such the non degenerate mode (associated with the truncated layer) can only propagate in the forbidden band. Consequently, the Bloch number K associated with this mode will be a complex number, meaning that the wave decays exponentially inside the PhC. At the same time, due to the fact that the wave also decays exponentially outside of the PhC, it will form a surface state, known as a BSW. The reflection spectrum of a 10 unit cell PhC is represented in Figure 2.23.

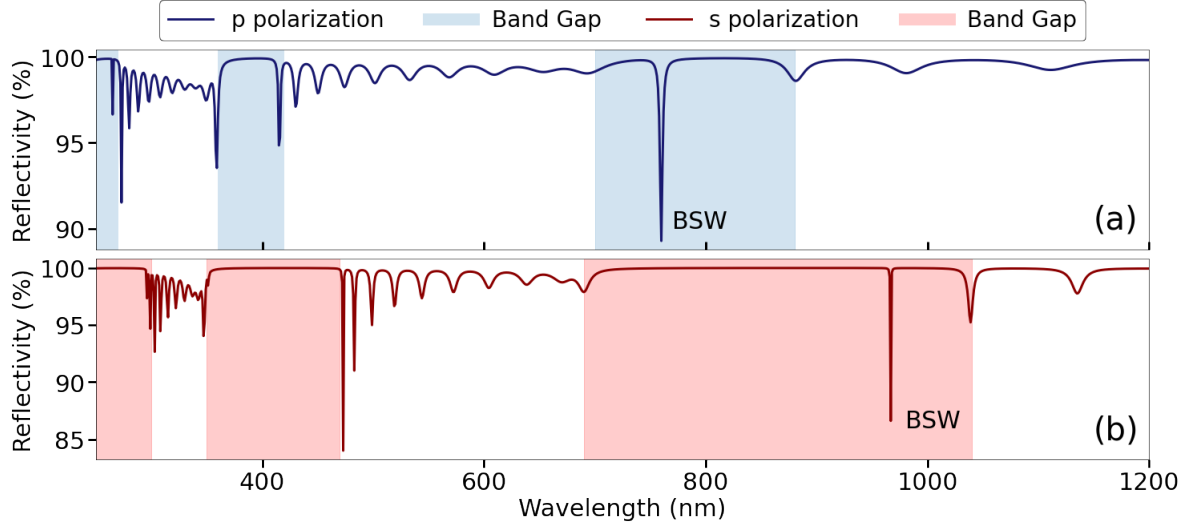


Figure 2.23: Reflection spectrum of a 10 unit cell PhC with a truncated layer, with $n_0 = 1.45$, $n_1 = 1.45$, $n_2 = 2.2$, $d_1 = 100\text{nm}$, $d_2 = 200\text{nm}$ and $d_s = 140\text{nm}$: a) s polarization, b) p polarization.

Figure 2.23 confirms of the BSW mode as a mode that propagates in the forbidden bands of the PhC, in which it can be seen that the mode propagates in a region that would otherwise have almost complete reflection. At the same time, in each allowed band a total of 10 modes is seen, corresponding to the non degenerate guided modes.

Figure 2.24 plots the transverse field of each BSW mode seen in Figure 2.23.

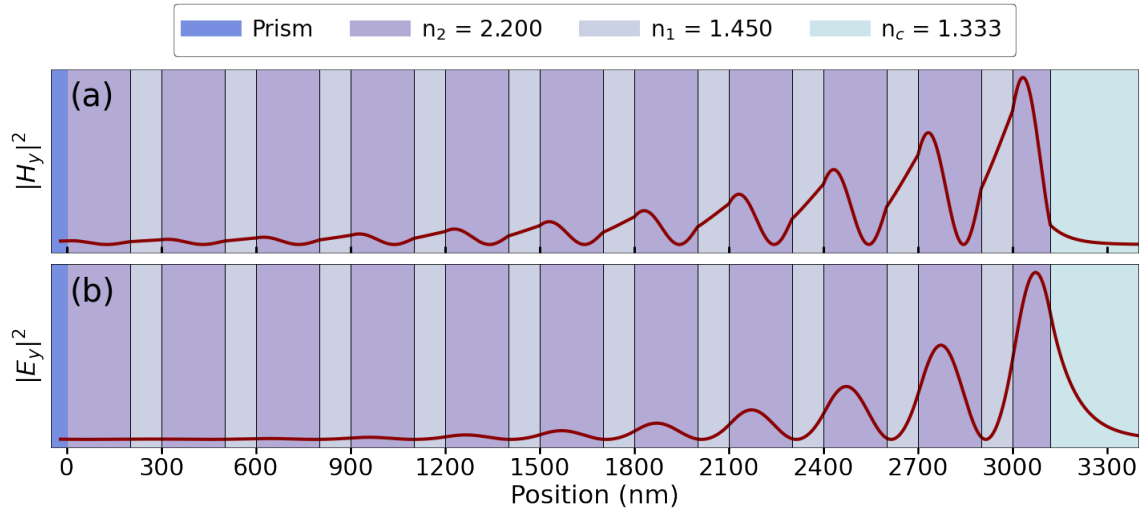


Figure 2.24: Transverse field profile of the BSW modes of a PhC with $n_0 = 1.45$, $n_1 = 1.45$, $n_2 = 2.2$, $d_1 = 100\text{nm}$, $d_2 = 200\text{nm}$ and $d_s = 140\text{nm}$: a) s polarization, b) p polarization.

Figure 2.24 allows the conclusion that the BSW is indeed a surface mode, where exponential decay away from the interface can be seen in both directions. Notice how the field is considerable amplified in the last layer, and a portion of the power associated with this mode travels outside

of the PhC, enabling sensor applications.

Characteristics of BSWs need to be studied numerically, making it hard to probe how each design parameter of the PhC interferes in the final mode. In particular, Yeh showed that for the appearance of BSWs a distance above a specific critical value between the high RI layers is needed, otherwise the mode is not generated [55]. A useful approach was developed by Martorell et al. [142], who were able to apply a semiclassical approximation to Equation 2.57 and show that the thickness of the last layer creates BSW modes with the same k_x for integer multiples of πk_{2z} , similarly to Schrödinger's equation where increasing the width of the potential well by half a wavelength produces a state of equal energy. This difficulty of finding explicit dependencies of BSW parameters from the PhC design is of particular nuisance for the design of PhC based devices such as BSW sensors, as will be seen in the following sections.

2.3.4 Physical Parameters of Bloch Surface Waves

Similarly to the approach in the study of SPPs, the physical properties of BSWs are here explained, showing how this ESW may be applied in different optical devices. As will be seen, this wave displays properties which in some aspects may be considered as opposite to SPPs, in particular due to the lack of losses in dielectric materials and the fast evanescent decay outside of the PhC.

Wavelength

Similarly to SPPs, BSWs display subwavelength confinement of light, but at a much reduced scale, especially when comparing with SPPs at lower wavelengths. Consider the PhC structure studied previously, which displays BSW modes in both s and p polarizations. The wavelength is obtained directly from the dispersion relation (Figure 2.22), where it can be seen that the BSW dispersion is always below the light line. This implies that for the same frequency of light, the BSW will have a higher k_x value, meaning that the wavelength of the BSW, defined as $\lambda_{BSW} = 2\pi/k_x$, will be inferior to the free space wavelength, as shown in Figure 2.25.

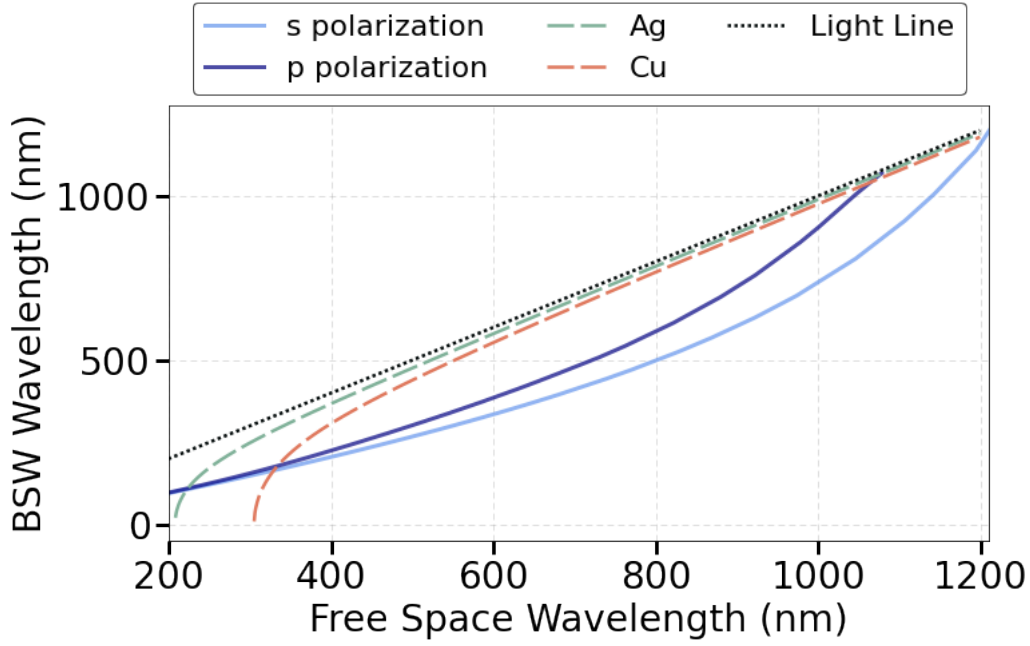


Figure 2.25: BSW wavelength as function of the free space wavelength. Comparison with a Silver and Copper SPP.

Also represented in Figure 2.25 is the wavelength confinement of a Silver and Copper SPP for comparison. It can be seen that at higher wavelengths BSWs display a higher confinement of light, due to the fact that in this region the SPP is light like. Nevertheless, the BSW wavelength seems to approximately follow the same trend of the light line, while SPPs display an extremely large improvement of light confinement near the frequency limit ω_s , where the SPP behaves similarly like a plasma. As such, plasmonic modes are generally more discussed in optical devices that take advantage of light confinement.

Propagation Length

While in SPPs the propagation length is mainly dictated by the losses in the metal, which cause an exponential decay of the wave along the direction of propagation, in the case of BSWs these effects are almost nonexistent. Generally speaking, dielectric materials have extremely low absorption and the surfaces are generally smooth, meaning almost no scattering losses are induced. Dubey et al. [143] found that in the case of the Kretschmann configuration, most losses are induced by leakage into the prism. This group deposited a PhC consisting of six unit cells composed of SiO_2 and SiN_x , which display an imaginary part of the RI of the order of 10^{-4} . By exciting the BSW using the Kretschmann configuration and collecting the near field using a scanning near field optical microscope, it was possible for the group to calculate the propagation of the BSW mode along the PhC surface, obtaining a value of 3.24 ± 0.13 mm, which is considerably higher than the propagation length of SPPs (as can be seen in Figure 2.7) and an order of magnitude higher than Long Range Plasmons [144].

Penetration Depth

As seen previously, the BSW decays exponentially away from the interface of the PhC with the external dielectric, similarly to the SPP. Two different situations exist in this case: the decay into the dielectric and the decay into the PhC. The first has already been implied in Equation 2.56, with the Penetration Depth being defined in this case as:

$$L_{BSW}^d = \frac{\lambda}{4\pi\sqrt{n_{ef}^2 - n_0^2}} \quad (2.58)$$

In the case of the decay inside the PhC, analysis of Equation 2.49 for the case of a BSW ($K \in \mathbb{C}$) that the Penetration depth can be defined as:

$$L_{BSW}^{PhC} = \frac{1}{2K_i} \quad (2.59)$$

Figure 2.25 compares the penetration depths of a PhC structure for the fundamental band gap in the two polarizations. The penetration depths of SPPs are also included for comparison.

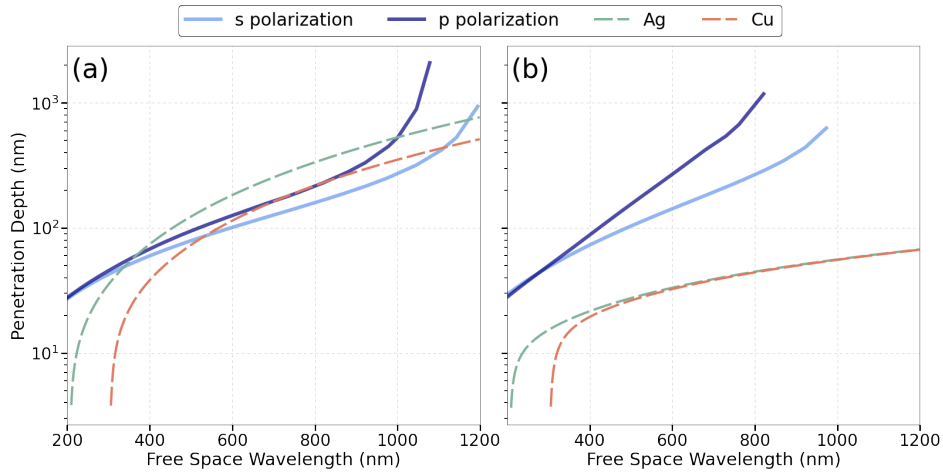


Figure 2.26: BSW penetration depth as a function of the wavelength: a) Penetration into the dielectric; b) Penetration into the PhC. Comparison with SPP for the case of Silver and Copper.

From figure 2.26 it can be seen that the penetration depth of BSWs into the dielectric is comparable to that of SPPs in the light like regime. It is interesting to observe that at high wavelengths L_{BSW}^d increases considerably, which is due both to the direct wavelength contribution (seen in Equation 2.58) and to the decrease of the effective index to values near n_0 . Regarding the penetration into the PhC, it can be seen that it is of the same order of magnitude of the penetration into the external dielectric, which is an opposite behavior to that of SPPs (where the field decays faster due to losses inside the metal). The fact that the field decay is similar on both sides of the interface bears important consequences in the sensitivity of BSW based optical sensors but also provides interesting possibilities, such as using porous materials in the PhC to

allow analyte penetration in the optical device, taking advantage of the considerable amount of power still inside the PhC [145].

2.3.5 Bloch Surface Wave based Sensors

Given the fact that a considerable portion of the power associated with BSW modes propagates on the external dielectric, these ESWs are sensitive to variations of the external RI, much like SPPs. This section focus on the theory behind BSW sensors, and some novel results are presented regarding the sensitivity of prism based devices. The same principles seen previously regarding the SPP sensors apply here, in particular the definition of sensitivity (Equation 2.37) and the FoM (Equation 2.44). Similarly to SPPs, we will consider excitation under the Kretschmann configuration, which is used in the experimental results section.

Prism Excitation of Bloch Surface Waves

Consider the Kretschmann configuration seen Figure 2.10, but with a truncated PhC on top of the structure. As seen previously, BSWs can only be excited by using a wavevector matching scheme, such as a prism. This configuration creates total internal reflection of light at the prism - PhC interface, thus coupling light to the BSW mode via evanescent field.

The principle behind BSW sensors is similar to that of SPPs, in particular that a change in the external RI (or molecule binding events in the functionalized surface) creates a change in the effective index of the mode that is translated into a shift in the peak wavelength of the band. This effect can be directly seen by calculating the dispersion relation of the structure in Figure 2.21 under different values of external RI, which is shown in Figure 2.27.

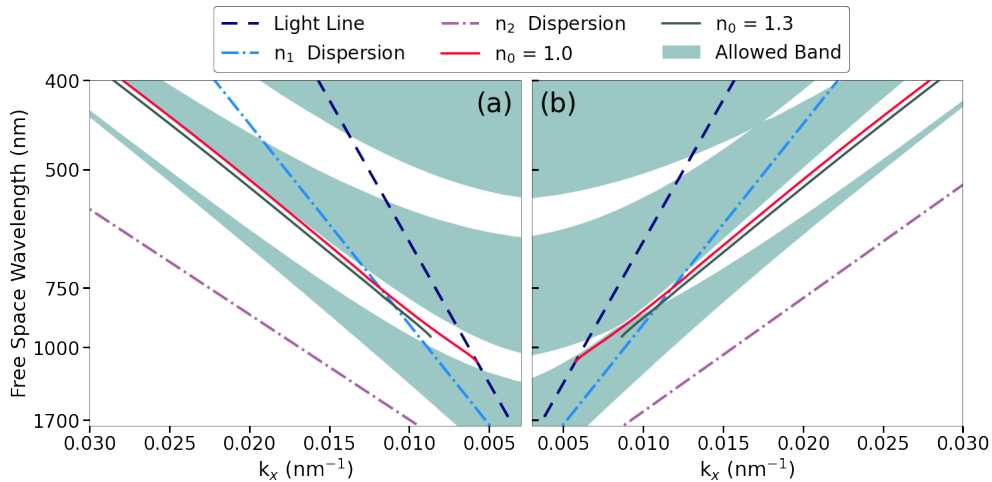


Figure 2.27: Dispersion relation of a semi infinite PhC with a truncated layer under various values of n_0 , with $n_1 = 1.45$, $n_2 = 2.2$, $d_1 = 100\text{nm}$, $d_2 = 200\text{nm}$ and $d_s = 140\text{nm}$: (a) s polarization; (b) p polarization.

From Figure 2.27 it can be seen that the variation of the external RI causes a redshift of the dispersion of all BSW modes, similarly to the effect in SPPs. BSW based sensors in the Kretschmann configuration rely on the crossing of the BSW dispersion line with the dispersion of the prism, thus registering a wavelength shift when the external RI is varied. The spectral dependence of the BSW effective index is plotted in Figure 2.28, and for different incidence angles the variation of the band peak is seen.

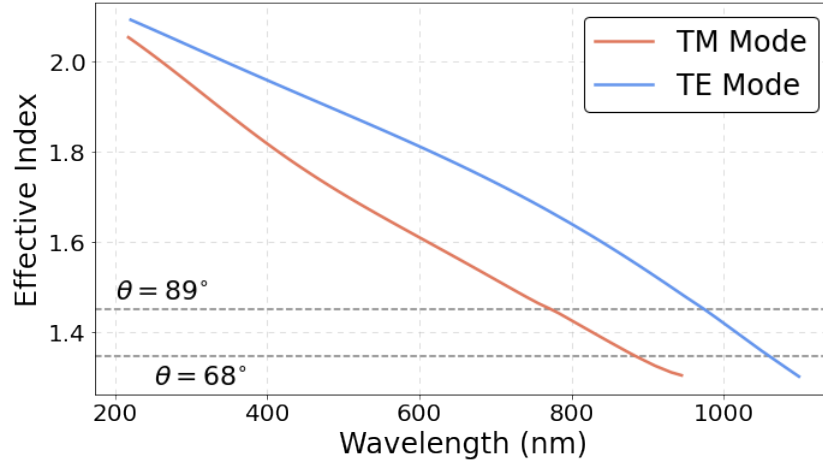


Figure 2.28: Spectral dependence of the effective index of BSW for different polarizations. The horizontal lines indicate the effective indices attained with a prism of $n_p = 1.45$, ranging from the critical angle to near normal incidence.

As can be seen in Figure 2.28, the peak wavelength position of the mode can be tuned by shifting the incidence angle of the experimental setup. This choice of angle has consequences in the sensitivity of the mode, as will be seen in the next section. Considering a prism of $n_p = 1.45$, the maximum value of effective index attainable is 1.45, and for higher values of n_{ef} a prism of higher RI is needed.

Sensitivity of Bloch Surface Waves

As mentioned previously, given the formal similarities between SPPs and BSWs, the sensitivity to external RI under the Kretschmann configuration is defined exactly in the same way, as seen in Equation 2.38. In particular, due to the shared method of ESW excitation, both the instrumental contribution and the effective index variation with the RI are defined similarly. In the instrumental contribution, the chromatic dispersion of the BSW mode can be calculated easily from the dispersion relation obtained numerically.

The sensitivity of the effective index of a BSW mode can be calculated using first order perturbation theory. The perturbation in the square of the effective index can be written as [133, 48]:

$$\Delta(n_{ef}^2) = \begin{cases} \frac{\frac{\lambda^2}{4\pi^2} \int_{-\infty}^{+\infty} \Delta\varepsilon(z) \left(\frac{1}{\varepsilon(z)} \frac{dH_y(z)}{dz} \right)^2 dz - n_{ef}^2 \int_{-\infty}^{+\infty} \Delta\left(\frac{1}{\varepsilon(z)}\right) H_y^2(z) dz}{\int_{-\infty}^{+\infty} \frac{1}{\varepsilon(z)} H_y^2(z) dz}, & \text{for TM Modes} \\ \frac{\int_{-\infty}^{+\infty} \Delta\varepsilon(z) E_y^2(z) dz}{\int_{-\infty}^{+\infty} E_y^2(z) dz}, & \text{for TE Modes} \end{cases} \quad (2.60)$$

By placing the field configurations of the BSW (Equations 2.49 and 2.56) in Equation 2.60, one can obtain the perturbation in the effective index using $\Delta(n_{ef}^2) = 2n_{ef}\Delta n_{ef}$. Two different kind of sensitivities should be explained. Firstly, the sensor will detect variations of the RI of the external dielectric, meaning that the device is used as a refractometer, and its sensitivity is referred as the refractometric sensitivity (RS). Lastly, the device can respond to variations of thickness of a very thin layer deposited on top of it, which is the principle behind affinity sensing (molecule binding increases this adlayer thickness). This second type of sensitivity is referred as the adsorption sensitivity (AS). Using the first order perturbation theory approach presented previously, these sensitivities were calculated analytically. For conciseness, the details of the calculations are included in the Appendix.

Refractometric Sensitivity In the case of the RS, consider a small perturbation to the external dielectric permittivity as $\varepsilon_0 = 2n_0 \Delta n_0$. The sensitivity to external RI is given by:

$$\frac{\partial n_{ef}}{\partial n_0} = \begin{cases} \frac{2n_{ef}^2 - n_0^2}{n_{ef}} \frac{1}{n_0 + 2n_0^3 q_0} \frac{P^{TM}}{|\alpha^2|}, & \text{for TM Modes} \\ \frac{1}{n_{ef}} \frac{n_0}{1 + 2q_0} \frac{P^{TE}}{|\alpha^2|}, & \text{for TE Modes} \end{cases} \quad (2.61)$$

where P^{TM} and P^{TE} are the power propagating inside the PhC for the TE and TM polarizations and α is the magnitude of the field at the interface between the PhC and the external dielectric (as defined in Equation 2.56). Figure 2.29 plots the dependence of the sensitivity of the effective index with the incident angle.

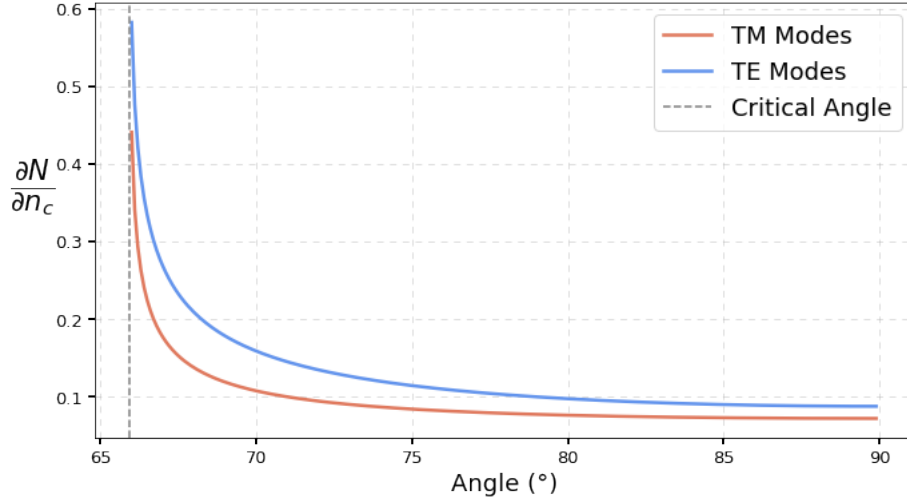


Figure 2.29: Sensitivity the effective index of TM and TE BSW modes for external RI variations as a function of the incidence angle assuming a ratio of $P/|\alpha|^2 = 500$.

Figure 2.29 shows that the sensitivity of TM modes is always higher than TE modes, although the same trend is seen for the two cases. It is interesting to observe a sharp increase in the effective index sensitivity near the critical angle, which happens for both polarizations. This effect, which is in agreement with previous publications [78], is explained by the fact that $q_0 = 2\pi/\lambda\sqrt{n_{ef}^2 - n_0^2}$, and at low angles the effective index is near the external index ($n_{ef} = n_p \sin(\theta_c) \approx n_0$), leading to an larger penetration depth and consequently a large part of the power associated with the mode propagating outside of the PhC.

In order to obtain the refractometric sensitivity, Equation 2.61 needs to be multiplied by the instrumental contribution, as defined in Equation 2.41. Figure 2.30 plots the RS of both TE and TM modes for a fixed value of $P/|\alpha|^2$.

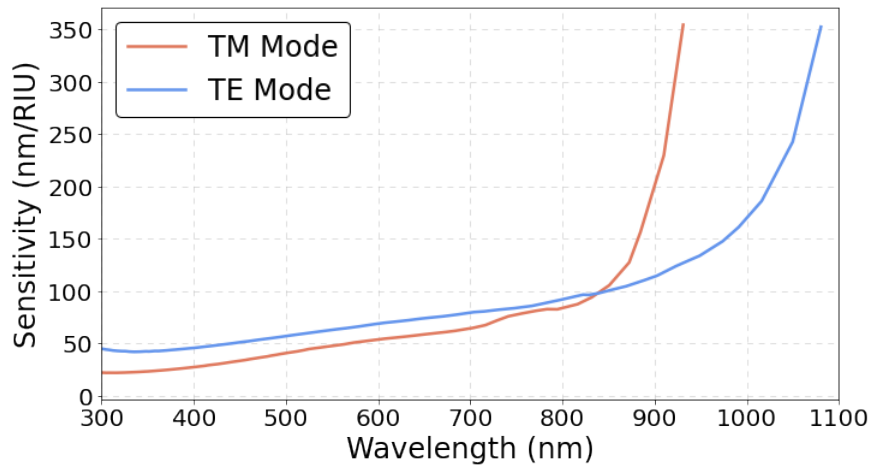


Figure 2.30: Refractive index sensitivity of BSW as a function of the wavelength for $P/|\alpha|^2 = 500$: a) TE modes; b) TM modes

As seen in Figure 2.30, an increase in wavelength leads to a higher sensitivity, which is explained by the increase in wavelength and decrease in the effective index, as stated previously. Notice that, from Figure 2.28, higher wavelengths are attainable by setting the incidence angle near the critical angle, also in agreement with Equation 2.61.

One interesting remark from the comparison of Figure 2.30 and Figure 2.13 is that the sensitivities of BSW's are considerably lower than the sensitivities of SPPs, even though the penetration depth is similar, as stated in Figure 2.26. This can be explained by Equations 2.60, which can be seen as a ratio of the amount of power associated with the mode that is in contact with the perturbation (the external dielectric RI variation) and the total power of the mode. In SPPs, the majority of the power is on the external dielectric, due to the fact that the decay into the metal is considerably faster (as seen in Figure 2.9), while in BSWs the power propagating inside and outside of the PhC is comparable because the decay length into the PhC is similar to that into the dielectric (Figure 2.26). This lowers the ratio of the perturbation theory approach and consequently deems the BSW mode as generally less sensitive than standard SPP approaches.

Adsorption Sensitivity In this case, consider a small adlayer of RI n_F and thickness d_F on top of the PhC cap layer. The permittivity perturbation will be the difference between the RI of this layer and the external dielectric, $\Delta\varepsilon = n_F^2 - n_0^2$. The perturbation of the effective index will be:

$$\frac{\partial n_{ef}}{\partial d_F} = \begin{cases} \frac{n_{ef}^2(n_0^{-2} + n_F^{-2}) - 1}{n_{ef}} \frac{(n_F^2 - n_0^2)}{\frac{1}{q_0} + 2n_0^2 \frac{P^{TM}}{\alpha^2}}, & \text{for TM Modes} \\ \frac{n_F^2 - n_0^2}{n_{ef}} \frac{1}{\frac{1}{q_0} + 2 \frac{P^{TE}}{\alpha^2}}, & \text{for TE Modes} \end{cases} \quad (2.62)$$

The study of the dependence of the sensitivity with the incident angle is plotted in Figure 2.29.

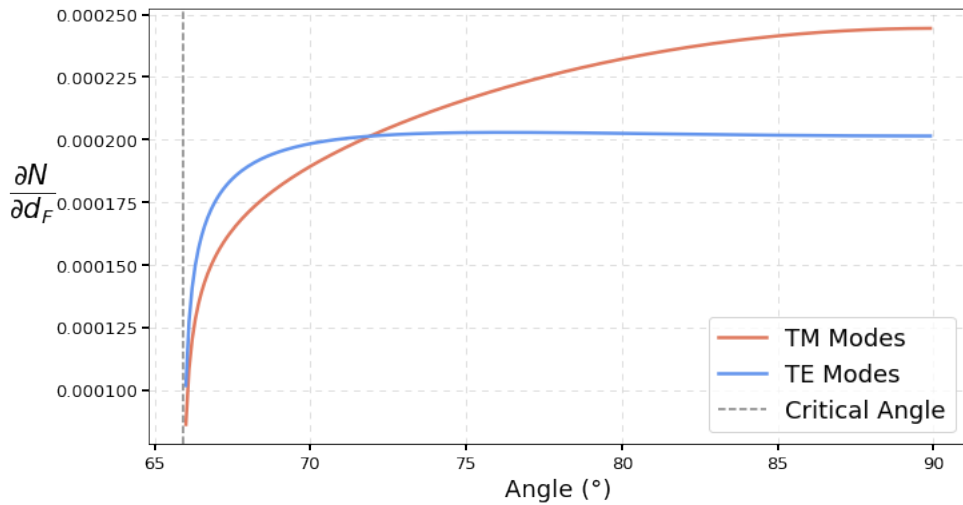


Figure 2.31: Sensitivity of the effective index of TM and TE BSW modes for adlayer thickness variations as a function of the incidence angle assuming a ratio of $P/|\alpha|^2 = 500$.

Analysis of Figure 2.31 provides the interesting observation that the dependence of the effective index sensitivity with the angle is opposite to that of the RS. The explanation for this relies on the fact that for adsorption sensitivity the field should be as confined to the near surface as possible, meaning that the propagation length should be minimized and q_0 should be maximized. This effect happens when the difference between the effective index and the external dielectric is high, which is achievable at higher angles, as shown in Figure 2.28.

Adding in the instrumental contribution, the peak sensitivity can be calculated, which is represented in Figure 2.32.

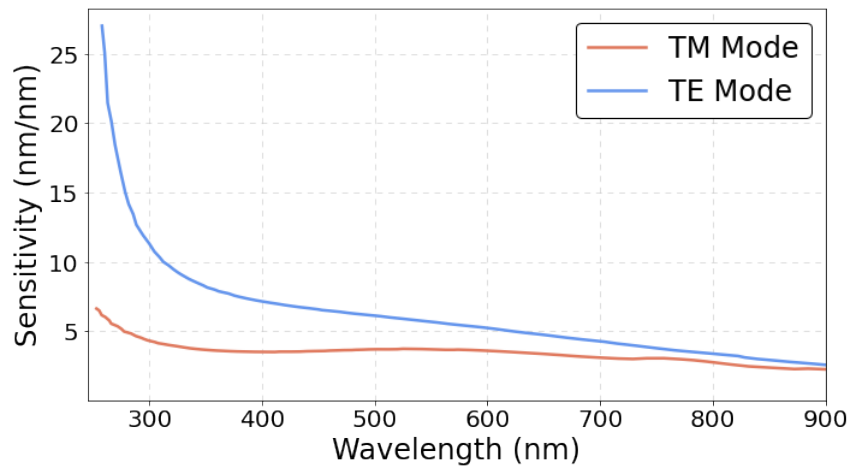


Figure 2.32: Adsorption sensitivity of TE and TM BSW modes as a function of the wavelength for $P/|\alpha|^2 = 500$.

From the analysis of Figure 2.32 it is possible to conclude that lower wavelengths should be used, which are achievable by higher angles. In this regime, light is mostly confined in the adlayer region, and sensitivity to molecule binding events will be higher. These results are in agreement with previous publications [146], in which BSW modes were employed in the ultraviolet range for high sensitivity using a total internal reflection ellipsometry setup.

Figure of Merit in Bloch Surface Wave Sensors

Given the similarities between SPPs and BSWs, in particular in their application to optical sensors, the performance of sensors can be evaluated using the same metrics. In BSWs the FoM (as defined in Figure 2.44) is also applicable and used to compare different configurations of BSW based optical sensors and also in comparisons with SPP based sensors.

The case of BSW sensitivity was analyzed previously, where it was seen that the sensitivity value is generally inferior to conventional SPP applications. Nevertheless, due to the lack of inherent losses, the FWHM of the modes is also reduced when comparing with SPPs, thus establishing interesting possibilities for high performance sensors.

Table 2.2 summarizes some results of recent implementations of BSW sensors under spectral interrogation, showing their sensitivity and FoM.

Table 2.2: Characteristics of experimental and simulated BSW based sensors under spectral interrogation schemes.

Device	Type	Materials	Sensitivity (nm/RIU)	FWHM (nm)	FoM (RIU ⁻¹)	Reference
Planar	Exp.	SiO ₂ / TiO ₂	751	29.7	25	[83]
D-shaped Fiber	Exp.	CuO / SnO ₂	322	52.5	6	[67]
Tapered Fiber	Exp.	Al ₂ O ₃ / TiO ₂	930	54.2	17	[86]
Planar	Sim.	Ge / ZnSe	1570	1.2	1869	[78]
Planar	Sim.	TiO ₂ / P-TiO ₂	9650	0.2	48250	[147]
Optical Fiber	Sim.	Ge / ZnSe	285	1.5	190	[148]

In Table 2.2 it is possible to observe a clear difference between the experimental and simulation results regarding BSW performance, in particular the FoM. The disparity in results stems from the fact that most implementations of BSW simulations fail to consider the experimental details, in particular the fact that collimation of light in typical Kretschmann configuration setups using spectral interrogation is not perfect (especially if the light is injected via fiber optics), creating a considerable broadening of the band that dramatically reduces the experimental value of the FoM. Such effect is not seen in angular interrogation setups, where light is coupled from a laser source (which can have an extremely narrow band) and high resolution platforms for stage rotation are available, thus achieving very narrow bands and consequently high sensor performance.

While plasmonic sensors may display better performance in the considered metrics, BSWs may still find application in contexts where SPP solutions perform poorly. Thin dielectric films generally form strong bonds between layers and have good adhesion to the substrate, making them extremely resistant to both physical and chemical damage [77]. This happens oppositely to the behaviour of many metal on substrate applications, where the metal may have poor adhesion (which is the case of Gold) [149] and/or may oxidize even when protected (as is the case of Silver, Gold and Aluminium) [150, 151]. Thus, BSWs may find application in extreme or corrosive environments, where plasmonic metals may not show the stability needed for optical sensing. At the same time, due to the FWHM stability even in increasing external RI value (as will be demonstrated in the results section), the FoM of these sensors is extremely stable, making them suitable to be used together with chemical functionalizations such as polymer cap layers. Although these functionalizations are also possible in SPR implementations, the FoM is drastically reduced if the external RI is similar to that of the substrate, making the fabrication of SPR chemical sensors a tricky process that requires thickness monitoring.

2.4 Metal-Dielectric Photonic Crystals

Having studied both SPPs and BSWs (along with the basic principles behind PhCs) we now advance towards structures that combine the two effects, called metal-dielectric photonic crystals (MDPhC). These optical devices combine metals and dielectrics within the unit cell, forming periodic lattices with different properties than conventional PhCs.

This section explores the properties of MDPhCs, from the formation of long and short range plasmons due to the interaction of SPPs of different interfaces within a metal layer and the formation of a plasmonic band. The excitation of ESWs in MDPhCs is then explored, explaining the new possibilities offered by these structures and the possibility of application in optical sensors.

2.4.1 Plasmonic modes on a metallic slab

Consider a system composed of a lossless metal layer with thickness d_m and permittivity ε_m , whose chromatic dispersion is given by the lossless Drude model, Equation 2.31 with $\gamma_p = 0$. This metal layer is surrounded by semi infinite media of permittivity ε_d . From the analysis made in section 2.2 it can be argued that two SPPs will form, one in each interface of the metal layer. In this case, both plasmons generated at each side of the surface are degenerate, meaning that their dispersion relation is the same because the interfaces are similar to each other. The transfer matrix $\mathbf{M}$ of the system is given by:

$$\mathbf{M} = M_{dm} P_m M_{dm} \quad (2.63)$$

For a simple system such as the one considered, analytic calculation of the existence of bound modes is possible, using Equation 2.24. In this case, the dispersion relation is:

$$e^{-2k_{mz}d} = \left(\frac{1 + k_{mz}\varepsilon_d/(k_{dz}\varepsilon_m)}{1 - k_{mz}\varepsilon_d/(k_{dz}\varepsilon_m)} \right) \quad (2.64)$$

Two solutions to Equation 2.64 can be derived, which consist of two different modes that propagate inside the metal layer. These solutions can be written as:

$$\begin{cases} \frac{1+k_{mz}\varepsilon_d/(k_{dz}\varepsilon_m)}{1-k_{mz}\varepsilon_d/(k_{dz}\varepsilon_m)} = -\tanh \frac{k_{zm}d_m}{2} \\ \frac{1+k_{mz}\varepsilon_d/(k_{dz}\varepsilon_m)}{1-k_{mz}\varepsilon_d/(k_{dz}\varepsilon_m)} = -\coth \frac{k_{zm}d_m}{2} \end{cases} \quad (2.65)$$

Equations 2.65 cannot be solved analytically and need numerical solving techniques. Figure 2.33 plots the solutions of these equations for various thicknesses of a lossless Drude metal.

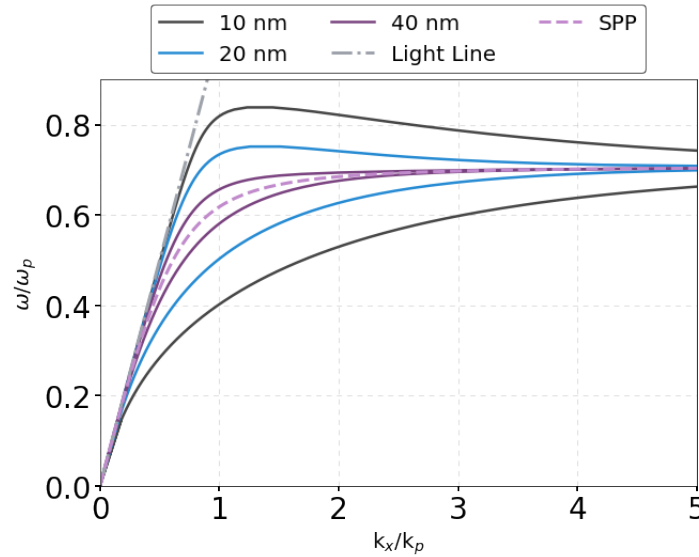


Figure 2.33: Dispersion relation of a metal layer of $\varepsilon_m = 1 - \lambda/\lambda_p$ ($\lambda_p = 145\text{nm}$), with $\varepsilon_d = 1$ for various metal values of d_m , under p polarized light. The original SPP mode at a metal dielectric interface is also represented.

From Figure 2.33 it can be seen that indeed two plasmonic modes are present, although their dispersion relations differ. Similarly to what was seen in Section 2.3 with the guided modes of the slab waveguide (which forms the PhC band due to the field interactions in different unit cells), a similar process is in the origin of the degeneracy lifting of the plasmonic modes of the metal layer. In this case, the plasmons generated at each surface interact inside the metal (where their fields overlap) creating a degeneracy lifting process that separates the plasmonic modes from the original SPP (also represented in Figure 2.33). This process is only visible in very thin metal layers due to the decay of the SPP mode inside the metal. Figure 2.33 shows this dependence with the metal thickness: for thicker metals ($>40\text{nm}$) the interaction between the fields is not as strong due to the decay of the field into the metal, consequently the modes are similar to the original SPP mode; for thinner metal layers the interaction between the modes at each interface becomes stronger and the degeneracy is considerably lifted, generating two different plasmonic modes. Similarly to the original SPP, both these modes tend to ω_s at high k values, but one does it from higher (ω^+) and another from lower frequencies (ω^-).

The classification of these new plasmonic modes stems from their tangential field profiles. Figure 2.34 plots these fields for the 30nm metal structure.

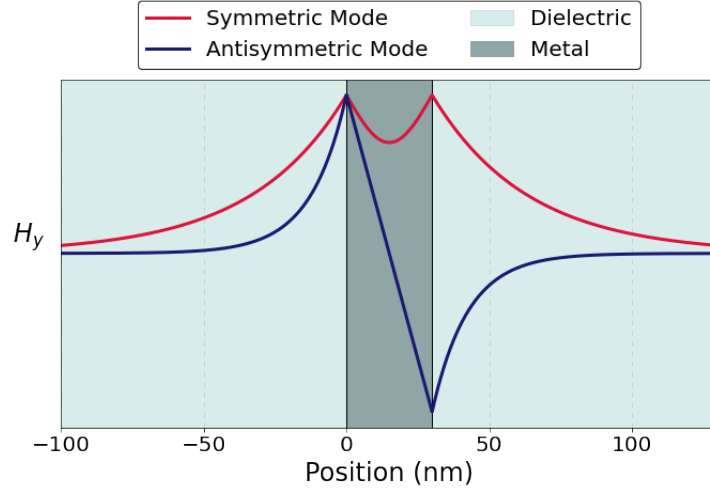


Figure 2.34: Tangential field profiles of the plasmonic modes of a metal layer of $d_m = 30\text{nm}$, $\varepsilon_m = 1 - \omega_p/\omega$ and $\varepsilon_d = 1$.

Figure 2.34 shows that the two fields have very different profiles, with one of them being symmetric and one antisymmetric in relation to the z axis⁶. As such, the ω^+ mode is called the symmetric mode and the ω^- mode is called the antisymmetric mode.

The most discussed property of these modes is their propagation length, which varies considerably in comparison with the SPP. It has been demonstrated that the symmetric mode displays extremely high propagation lengths, even reaching the centimeter scale [152], while the antisymmetric modes are more attenuated than even the conventional SPP [127]. While many explanations for this difference have been presented, the simplest one is that the penetration depth of the symmetric mode into the dielectric is higher than that of the antisymmetric mode (as seen in Figure 2.34), meaning that a larger portion of the power propagates in the dielectric, where there are less losses. This means that the mode will be less attenuated, thus justifying the higher propagation length. For this reason, the symmetric and antisymmetric modes are generally referred to as long and short range plasmons, respectively [152, 153].

The fact that long range plasmons (LRSPPs) display higher penetration depth and propagation length makes them ideal for sensor applications due to the higher portion of power that interacts with the external dielectric and the larger interaction length. Several sensors have been employed to explore this mode [137, 154, 155] and excellent results were shown, largely surpassing the performance of typical SPP implementations.

⁶The notation on which mode is symmetric and antisymmetric is not universal, as is discussed by Solymar et al. [127]. While some authors classify the modes by their tangential field component, some prefer the transverse field component (due to symmetries of the charge distribution in the surfaces). In this work we follow the former choice due to the relation with the magnetic field.

2.4.2 Metal-Dielectric Photonic Crystals: Unit Cell

Similarly to the approach adopted in section 2.3, we start by exploring this type of PhC by studying the properties of a single unit cell, considering two dielectric layers of permittivity ϵ_d and thickness d_d surrounding a metal layer of permittivity ϵ_m and thickness d_m . Figure 2.35 illustrates this structure.

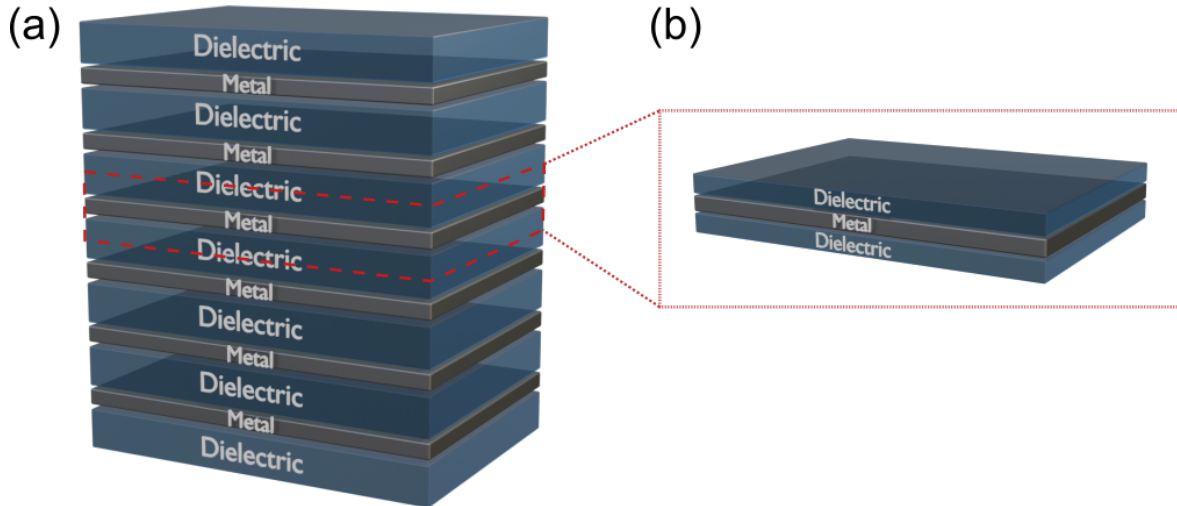


Figure 2.35: Illustration of the structure of a 1D MDPHC: (a) Complete crystal; (b) Unit cell.

In analysing the structure of Figure 2.35, consider again a lossless metal. While for some metals this approximation may induce large errors, for the case of plasmonic metals (especially Silver) it remains a reasonable assumption in the visible and infrared parts of the spectra.

As seen previously, the unit cell of Figure 2.35 shows two metal-dielectric interfaces, which under specific conditions may excite SPPs. In addition to the plasmonic modes, guided modes may also be present depending on the thicknesses and refractive indices of the dielectric layers, because these may function as waveguides. Figure 2.36 illustrates the dispersion relation of this unit cell, considering a fixed permittivity of $\epsilon_d = 4.84$ for the dielectric, the lossless Drude model with $\lambda_p = 145\text{nm}$ for the metal (to compensate for the very dispersive behaviour of metals), $d_d = 100\text{nm}$ and $d_m = 20\text{nm}$.

Figure 2.36 can be analysed in light of what was observed for guided modes in PhCs and the plasmonic modes in two interfaces of a metal layer. For the s polarization, guided modes are present in the dielectric layers and their degeneracy is lifted due to the fact that the fields interact inside the metal layer. Therefore, the modes of the single slab layer of permittivity $\epsilon_d = 4.84$ are transformed into two non-degenerate modes forming the TE and TM modes indicated in Figure 2.36. At the same time, in the p polarization it is also possible to observe the existence of two plasmonic modes, which correspond to the short and long range plasmons (SRSPP and LRSPP, respectively) discussed previously.

Analysis of the dispersion relation in Figure 2.36 shows that in the case of the guided modes

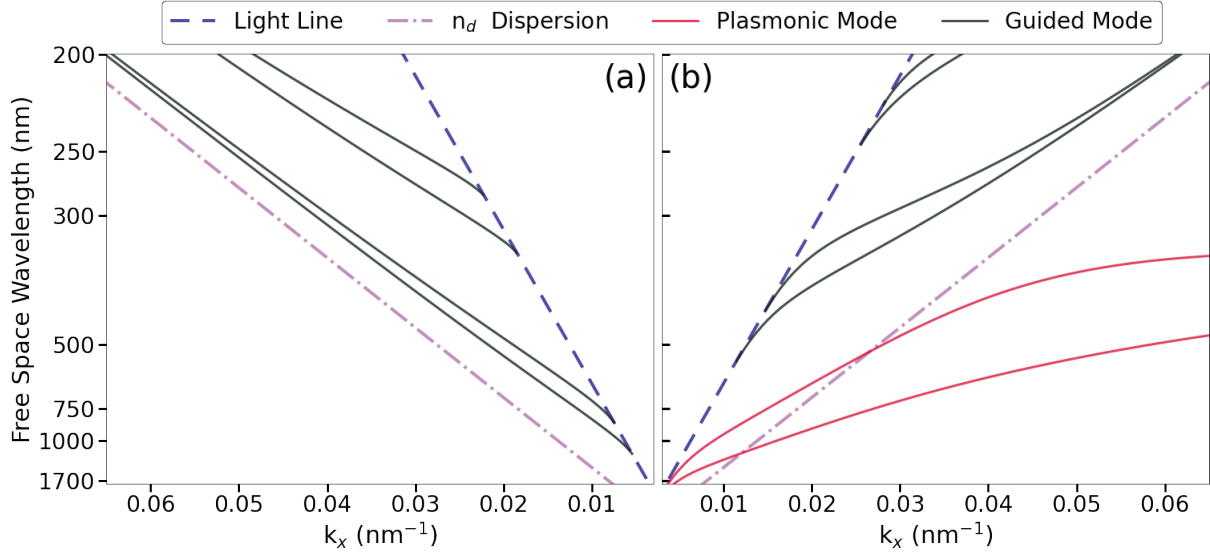


Figure 2.36: Dispersion relation of a unit cell of a MDPHC, with $d_d = 100\text{nm}$, $d_m = 20\text{nm}$, $\varepsilon_d = 4.84$ and $\varepsilon_m = 1 - \omega_p^2/\omega^2$, with $\omega_p = 145\text{nm}$: (a) s polarization; (b) p polarization.

the unit cell behaves much like an all dielectric unit cell, except for the inclusion of plasmonic modes in the p polarization. As such, it can be predicted that the case of the infinite MDPHC will bear similarities with the all dielectric PhC, in particular in the appearance of allowed and forbidden bands of light propagation.

2.4.3 Metal-Dielectric Photonic Crystal: Infinite case

We now tackle the problem of modelling a system composed of multiple unit cells, from two to the infinite case. Such a problem has been approached by several authors [156, 100, 157], and is still an ongoing field of research for optical device fabrication [99]. Given that we are dealing with a lossless metal, Bloch's Theorem and all the derivations presented previously (Equations 2.49 to 2.53) are still applicable in metal-dielectric periodic structures and will not be repeated here. The analysis of section 2.3 will serve as the basis for the analysis of metal dielectric systems.

Consider a system of four unit cells similar to that of Figure 2.35 stacked together. As seen previously, each mode of the dielectric layer will originate new non-degenerate modes, creating allowed bands of light propagation. The interesting property of metal dielectric structures is the interaction between the different plasmonic modes within each metallic layer. Figure 2.37 shows the dispersion relation for this structure.

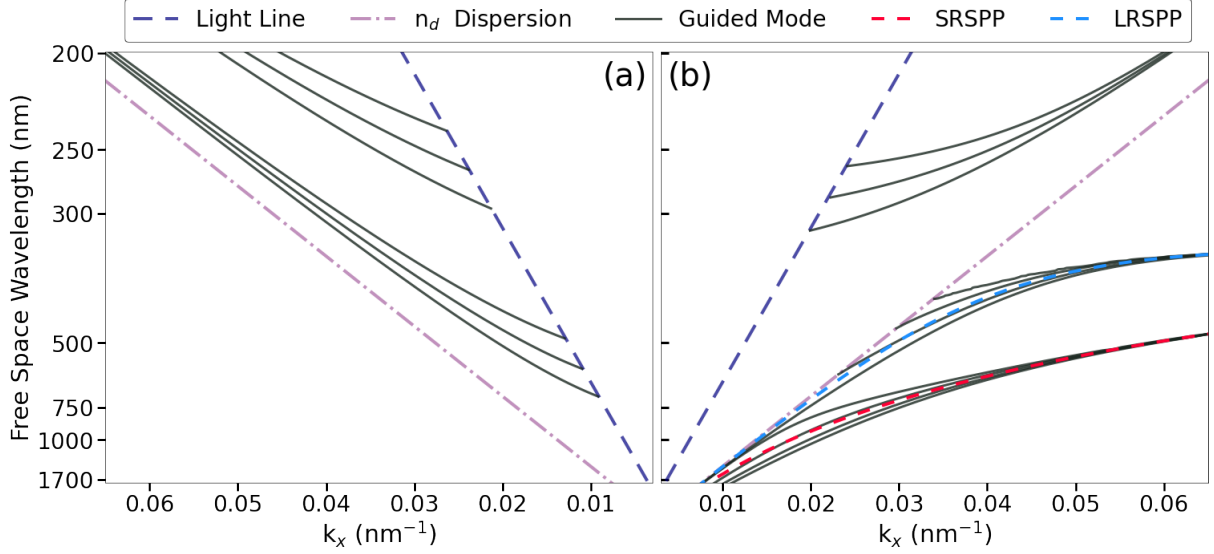


Figure 2.37: Dispersion relation of 4 unit cells of a MDPHC, with $d_d = 100\text{nm}$, $d_m = 20\text{nm}$, $\varepsilon_d = 4.84$ and $\varepsilon_m = 1 - \omega_p^2/\omega^2$, with $\omega_p = 145\text{nm}$: (a) s polarization; (b) p polarization.

From Figure 2.37 it can be seen that the guided modes behave as expected, meaning the formation of bands is clearly seen, similarly to what was verified in Section 2.3. The interesting observation is that the plasmonic modes from different metal layers also interact with each other, leading to a similar splitting of both the original LRSPP and the SRSPP, which by themselves were already the result of a splitting of the original SPP. This process of band formation in metal dielectric periodic structures forms the basis behind high-k modes in hyperbolic metamaterials [156], and the modes are referred to multilayer, volume or Bloch plasmon polaritons (BPP) [157].

The physical process behind the formation of Bloch plasmons is a matter of discussion in several publications. While Zhukovsky et al. [158] argue that the formation of these modes stems from coupling of SRSPPs within the metal layers (while arguing that LRSPPs do not form a high k band), Rosenblatt et. al [159] show that two bands are formed, one composed of gap modes (gap plasmons) and one composed of slab modes. Gap modes couple and propagate inside the dielectric layers, and correspond to the coupling of LRSPPs, while slab modes correspond to the coupling of SRSPPs and propagate mostly within the metal layers. In Figure 2.37 this situation is tackled by plotting the dispersion relation of a single metal slab of thickness $d_m = 20\text{nm}$, and it is possible to observe that the plasmonic bands generate from the LRSPP and SRSPP originated by the single metal slab, in agreement with [159].

As stated previously, analysis of this system can be done using Bloch's Theorem, in particular Equation 2.51 is still applicable in this case. Figure 2.38 illustrates the case of the infinite PhC case along with the calculation of the Bloch number K .

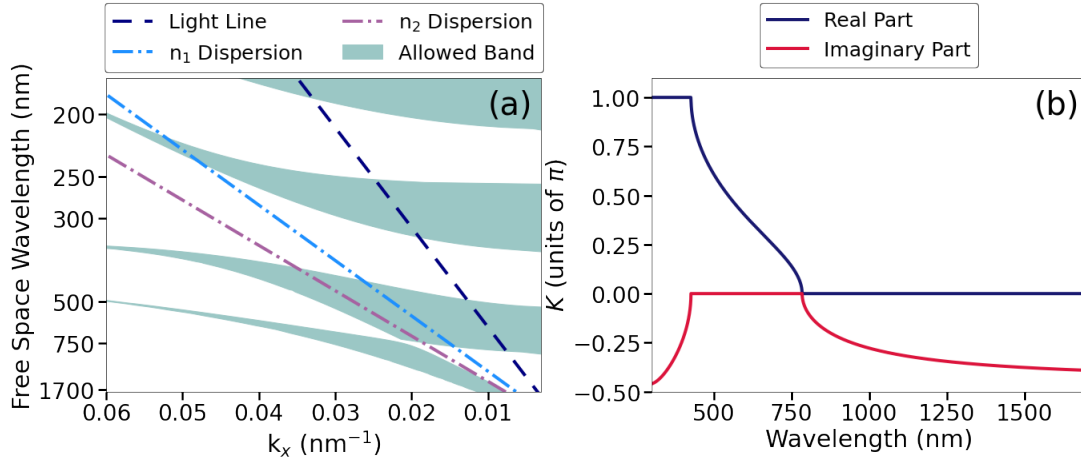


Figure 2.38: PhC structure (for the 4 unit cell and infinite case) with $d_d = 100\text{nm}$, $d_m = 20\text{nm}$, $\varepsilon_d = 4.84$ and $\varepsilon_m = 1 - \omega_p/\omega$, with $\omega_p = 145\text{nm}$: (a) Dispersion relation for the s polarization; (b) Bloch Wave number as a function of the wavelength along the dispersion of n_1 .

Figure 2.38 shows that the plasmonic modes form a band where $K = m\pi + iK_i$, similar to guided modes of all dielectric PhCs. This analysis confirms that in lossless metal-dielectric structures the plasmonic modes correspond to Bloch waves, similarly to guided modes in dielectric PhCs. Thus, the applicability of Bloch's Theorem is demonstrated, which continues to serve as basis for design and interpretation of metal-dielectric periodic structures.

A necessary observation in metal dielectric structures regards the losses in the system induced by the metal absorption. While noble metals display relatively low losses, this is still a limiting factor in device design [101], and any realistic implementation must account for this effect, meaning that the number of unit cells is limited. Another note is that due to the very high k values shown by the plasmonic band, excitation of these modes is not a trivial task due to the need to match the wavevector. Avrustky et al. [100] were able to experimentally demonstrate the excitation of Bloch plasmons using a Silicon prism, which has an extremely high RI ($n_p = 3.48$ at n_D). Sreekanth et al. [37] were also able to observe BPP modes by inciding light on a metal dielectric structure (forming a hyperbolic metamaterial) covered by a hypergrating, which consists of a PMMA grating structure covered by a 20nm layer of Ag, which is used to match the high wavevector needed for BPP mode excitation.

2.4.4 Metal-Dielectric Photonic Crystal: Truncated case

Having studied the formation of bands stemming from both guided and plasmonic modes of an MDPHC, the case of a truncated MDPHC is now tackled. In this case the last layer is composed of the same dielectric as the bulk of the MDPHC but with inferior thickness $d_s = 40\text{nm}$. Figure 2.39 illustrates the structure considered.

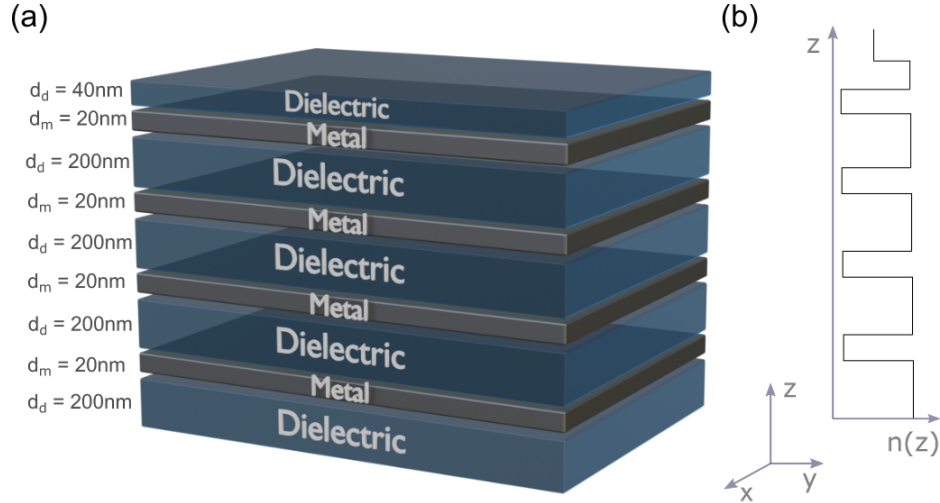


Figure 2.39: Truncated MDPHC structure, displaying four unit cells and a truncated cap layer. The parameters considered were $d_d = 100\text{nm}$, $d_m = 20\text{nm}$, $d_s = 40\text{nm}$, $\varepsilon_d = 4.84$ and $\varepsilon_m = 1 - \omega_p/\omega$, with $\omega_p = 145\text{nm}$.

The structure presented in Figure 2.39 displays an interesting configuration of metal dielectric layers. While the bulk of the PhC will display guided and plasmonic modes, the truncated layer creates a perturbation to the periodicity which may induce the appearance of BSWs, similarly to what was seen in all-dielectric PhCs. Figure 2.40 shows the dispersion relation of this structure.

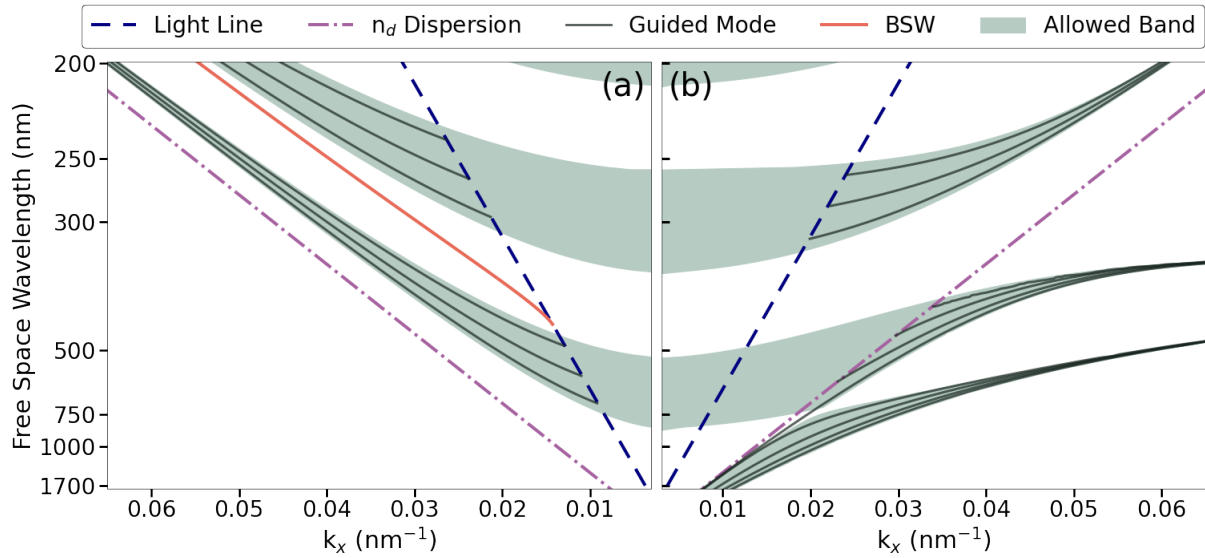


Figure 2.40: Truncated PhC structure with four unit cells and a truncated cap layer, with $d_d = 100\text{nm}$, $d_m = 20\text{nm}$, $d_s = 40\text{nm}$, $\varepsilon_d = 4.84$ and $\varepsilon_m = 1 - \omega_p/\omega$, with $\omega_p = 145\text{nm}$: a) s polarization; b) s polarization

From Figure 2.40 it can be seen that the inclusion of a truncated layer induces the same effect as in dielectric PhCs, meaning that BSW's can be excited in metal-dielectric PhC's as well. In the s polarization a mode can be seen propagating between the fundamental and the first bands,

corresponding to a BSW mode very similar to the case of conventional PhCs.

The case presented implies that the simultaneous excitation of (at least) two surface waves is possible in MDPhCs, with one of them being a BSW and another being a plasmonic mode. While it can be argued that the plasmonic modes are not a true surface mode (generated at the surface and decaying exponentially), as seen in Figure 2.20, reducing the number of unit cells will lead to an increased penetration of the mode outside of the device, working as a surface wave. This possibility may present interesting opportunities in waveguiding and optical sensor devices, due to the fact that two different surface modes (along with guided modes) can be chosen by shifting polarization of light, introducing a new degree of flexibility in these devices. In the particular case of optical sensors, the possibility of designing surface modes at opposite ends of the spectrum (in the structure presented in Figure 2.40, an *s* polarized BSW exists in the UV range and plasmonic modes exist in the infrared) may allow tailoring of the surface modes to respond differently to external variations of RI or molecule coupling in the surface by displaying very different penetration depths, creating new possibilities in the field of optical sensing.

Chapter 3

Materials and Methods

Simulation and experimental methodologies used in the design and fabrication of ESW supporting devices are presented in the following sections. This process relies on three main steps: simulation of the 1D structure, deposition/fabrication of the film stack and characterization of the device. Firstly, the technique used for deposition of thin films is explained, along with optimization of the deposition procedure and the results of the system calibration. Then, the experimental setup for ESW excitation is presented, showing how light was coupled to the multilayer structures and how the characterization of the devices as sensors was made. Lastly, the computational implementation of the transfer matrix formalism presented in Section 2.1, which was used throughout this work due to the capability of accurately modelling the optical response of 1D stacks of metals or dielectrics, is here described. As will be seen, the software was adapted to accurately simulate the experimental setup (by incorporating angular broadening), justifying the presentation in the last section of this chapter.

3.1 RF Magnetron Sputtering Deposition of Thin Films

Deposition of the thin films that constitute the multilayer stacks developed in this work was done by Radio Frequency (RF) Magnetron Sputtering, which is a physical vapor deposition technique that allows fabrication of both metal and dielectric films. A part of the work developed regarded the improvement and optimization of the sputtering system, which is explained in this section.

3.1.1 Description of the Sputtering System

RF magnetron sputtering technique consists in generating plasma using an RF voltage (at 13.56MHz), which ionizes Argon molecules inside the chamber. Due a large voltage difference, these atoms accelerate towards the cathode and hit the target to remove the desired material, which is then deposited in the substrate. Figure 3.1 presents a basic illustration of the components involved in the sputtering system.

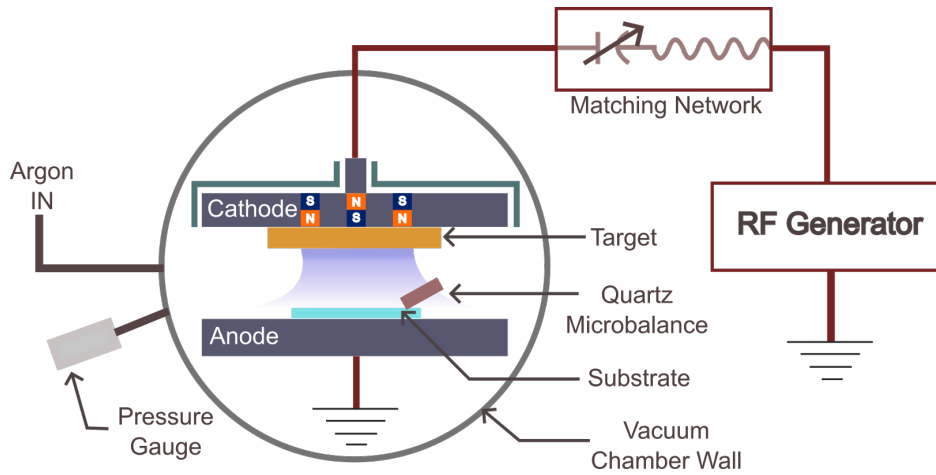


Figure 3.1: Illustration of the basic components of an RF Magnetron Sputtering.

The Argon ions are attracted by the large potential at the cathode and display energies generally in the range of 0.5 to 3 KeV, thus bombarding the target at an energy several times that of the activation energy for evaporation [160]. Thus, the target material is vaporized and deposited in the substrate, creating a slow process (approximately at the rate of one atomic layer per second) of thin film deposition. The most important components in the sputtering setup are illustrated in Figure 3.1 and shown in Figure 3.2, which consists of the RF Magnetron Sputtering setup currently available in the INESC-TEC facilities.

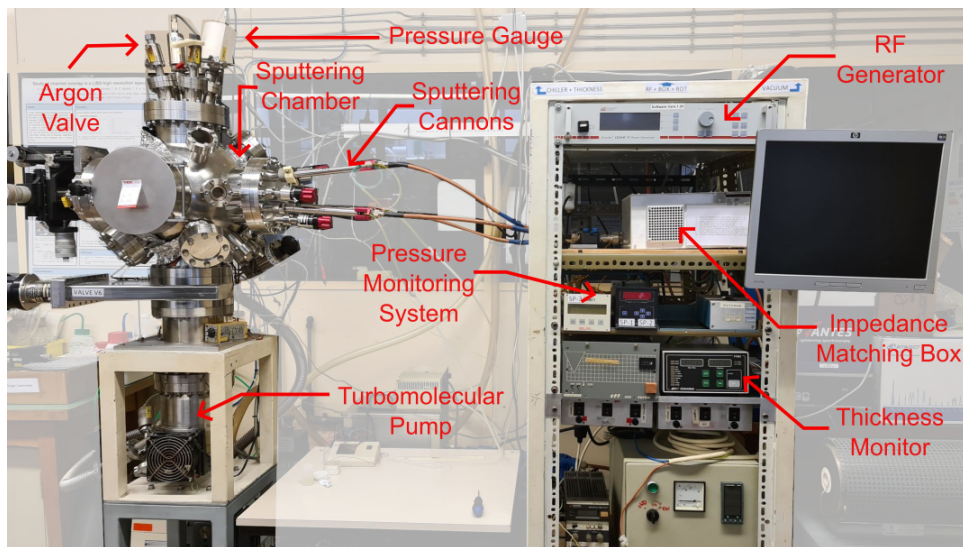


Figure 3.2: RF magnetron sputtering system used for the deposition of the multilayer structures.

The RF voltage is generated by an RF generator (CESAR RF Power Supply model 1312), connected to an impedance matching network (Advanced Energy Industries VM600A). The impedance matching network is needed to ensure that the power generated is totally transmitted to the sputtering target, and no reflection exists. Due to variations of pressure and temperature inside the chamber the impedance varies with time, thus justifying the need for the matching

network, to prevent damage in the RF generator caused by a reflected wave. The length of the transmission cables between the generator and impedance network, which depends on the wave speed in the cable and the frequency, was also adjusted to minimize reflection. Thus, the RF voltage is generated, and a magnetron is used to force the electrons into helical paths, increasing the probability of collision and ionization of an Ar atom. At the same time, the magnetron redirects the secondary electrons (generated by the ion bombardment in the target) to the ground shield, preventing them from hitting the substrate [160].

Vacuum is created in the stainless steel chamber by first connecting it to a primary pump (Edwards RV12), which lowers the pressure to $\sim 10^{-3}$ mbar. Then, the chamber is connected to a turbomolecular pump (Alcatel-Annecy 5400) supported by another primary pump, which allows an ultimate base pressure of $\sim 10^{-7}$ mbar. Two pressure gauges were installed in the setup, one inside the chamber (Adixen ACS 2000) and another between the turbomolecular pump and the supporting primary pump. The pressure gauge on inside the chamber is consists of both a Pirani gauge (for pressures higher than 10^{-2} mbar) and a Penning gauge (for pressures lower than 10^{-2} mbar), and switches automatically between the two depending on the pressure value. The pressure gauge between the turbomolecular and primary pump is a Pirani gauge. Insertion of the Argon gas is made by a precision valve connected to a gas cylinder, which allows pressure regulation. Given that in sputtering processes approximately 75% of the energy is dissipated as heat in the target [160], a water cooling system is also used for refrigeration, which was set at 10°C .

Three sputtering sources (Meivac MAK 2") are available, indicated in Figure 3.2. Due to previous damage, one of the sources can only support low power and is used for adhesion layers, which are generally very thin (below 5nm) metallic layers composed of Chromium or Titanium. The other sources are used for deposition of the multilayer materials, whether they are dielectric or metals. The three sputtering sources allow for multilayer structures of three materials (with the referred limitations to one of them) and are connected with a switch to the impedance matching box, allowing an easy change of material to deposit.

Figure 3.1 illustrates the deposition of films on a planar substrate. Nevertheless, modifications were made to the sputtering chamber in order to allow deposition in optical fibers as well. The fiber is set at approximately 5cm of the target and is rotated inside at a constant rate by a motor connected to a current source, thus depositing uniformly around the fiber core.

3.1.2 Calibration of the Sputtering System

Given that the quartz crystal microbalance used in thickness monitoring is not directly aligned with the material jet caused by the Ar ion collisions (as shown in Figure 3.1), calibration of the system was needed in order to fabricate films of controlled thickness. Even though the three target holders are equidistant from the substrate holder, the quartz microbalance isn't, requiring a different calibration for each sputtering source. This calibration was made by producing a metal dielectric layered structure with fixed thicknesses read by the thickness monitor (75nm).

The films were then cleaved and taken to Scanning Electron Microscopy (SEM) analysis, which allows a visualization of the profile structure of the films.

The choice of a metal dielectric structure for SEM analysis (composed of Chromium and SiO_2 , each layer with 75nm) was made to provide the necessary contrast in the images. Dielectrics display poor conductivity and consequently the SEM images show poor contrast between dielectric layers, which is not ideal for thickness measurement. Thus, multiple metal dielectric stacks give the necessary contrast and allow many thickness measurements (one per layer), establishing a calibration factor for each sputtering source (called the tooling factor) and an uncertainty associated with every layer. Thickness measurements of the SEM images was made by using ImageJ [161] along with a length scale provided by the SEM software. While both secondary electrons (SE) and backscattered electrons (BSE) images were taken, BSE images provide a clearer visualization of the limits between layers.

This calibration process was made in a total of four substrates, two planar SiO_2 substrates and two multimode optical fibers (MMFs). Two substrates of each type were chosen in order to repeat the process by changing the metal and dielectric targets from the target holders (TH): first the Cr target was placed in TH_1 and the SiO_2 was placed in TH_2 , then this process was repeated by changing the materials in the THs. This ensured that there was no dependence of the type of material with the thickness value. Figure 3.4 shows the result of SEM analysis for a planar substrate and an optical fiber.

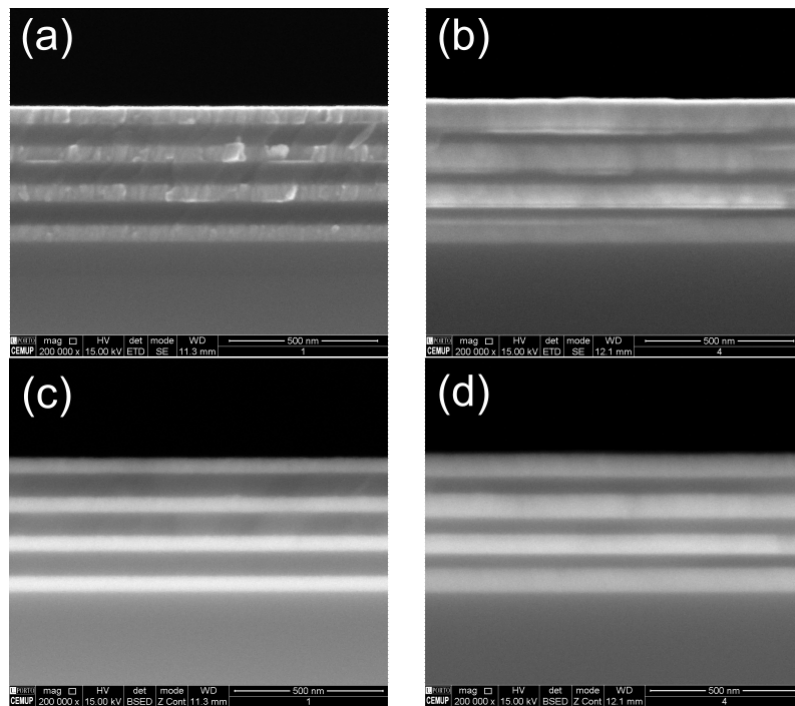


Figure 3.3: SEM analysis of the metal-dielectric layered structure used for calibration: (a) Cr in TH_1 , SiO_2 in TH_2 , SE; (b) Cr in TH_2 , SiO_2 in TH_1 , SE; (c) Cr in TH_1 , SiO_2 in TH_2 , BSE; (d) Cr in TH_2 , SiO_2 in TH_1 , BSE.

As can be seen in Figure 3.3, the target holder influences greatly the thickness of the film, and it can be seen that TH₂ consistently has an increased thickness. Thus, two tooling factors (one for each target holder, excluding the damaged one) were calculated. Figure 3.4 plots the results of the calibration analysis.

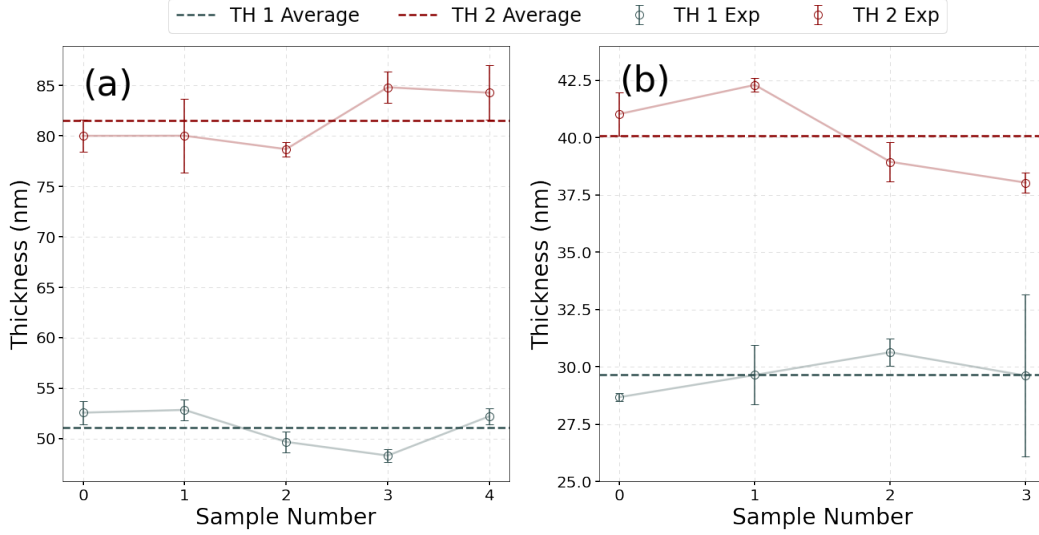


Figure 3.4: Calculation of the thickness deposited in each sample: (a) Planar substrates; (b) Multimode Optical Fibers.

Figure 3.4 shows that although there is some variation between different samples, the results from different depositions remain relatively stable (under 5nm thickness variation for each 75nm layer). This variation in the measured thicknesses may also be caused by differences in the position of the samples, due to the fact that the deposition may not be isotropic along the length of the substrate or fiber. For each case, the average of the thickness measurements was taken and the tooling factor was calculated as $TF = 75/t$, where t is the average thickness for each target holder.

3.1.3 Optimization of the Sputtering System

While in both ESWs studied the quality of the films deposited should be an important factor, the effect of film quality is of extreme importance in SPPs. Due to the fact that the plasmonic effect is heavily dependent on the collective motion of free electrons in metals, the absence of scattering effects in metallic films increases the quality of the plasmonic resonance [162]. In particular, in order for metallic films to display the highest quality possible, high deposition rates and high values of Ar base pressure should be used to guarantee large grain sizes [163], minimizing grain boundary effects.

Improvements were made in the sputtering chamber to improve metal film quality and to increase deposition rate of dielectrics, which would not increase above 0.03nm/s due to a large distance between the substrate holder and the targets. This distance was decreased from 20 to

8cm (allowing higher deposition rates), and higher values of pressure and power were employed (to 8×10^{-2} mbar and approximately 15W for metals and 110W for dielectrics). Changes were also made to the Ar injection system, which was placed further from the targets to increase uniformity of the gas inside the chamber. A silicone rubber heating tape was also added for vacuum chamber heating, and a decrease in pressure of about an order of magnitude was achieved. Figure 3.5 compares the results of depositions of metal dielectric multilayer (Cr-SiO₂) structures before and after the optimization of the sputtering chamber.

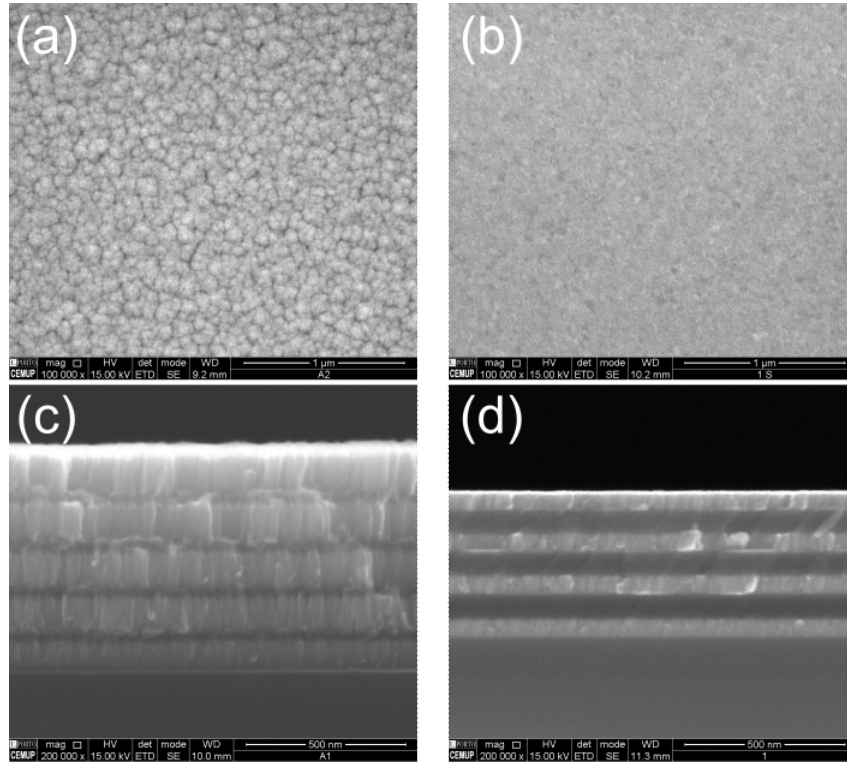


Figure 3.5: SEM analysis of two different metal-dielectric stacks: (a) Before optimization, surface image; (b) After improvements, surface image; (c) Before optimization, profile image; (d) After improvements, profile image. Notice that while the structures have different thicknesses, an improvement in the roughness of the deposition after the changes in the sputtering chamber is clearly seen.

Figure 3.5 that even though the structures have very different thicknesses, clear improvements are observed after the changes made in the sputtering chamber. While sputtering techniques lead to columnar growth of films [77], the size of these grains was increased, which improves significantly plasmonic behaviour [164, 162]. At the same time, the surface roughness was notably decreased, which was also shown to improve plasmonic behaviour by minimizing damping effects [165]. These modifications were of particular importance in the development of very thin plasmonic films (below 50nm, such as those in Section 4.3), where the film thickness is of the same order of magnitude as the mean free path of electrons, and damping effects become significantly more intense.

3.1.4 Thin Film Deposition

In the case of planar geometry, the fabricated structures were deposited on SiO₂ substrates, which match the SiO₂ prism. The substrates were cleaned in the Clean Room facility of CEMUP (Centro de Materiais da Universidade do Porto) according with the following protocol: firstly, the substrates were placed in acetone under ultrasonic bath for 10 minutes, after which they were soaked in isopropyl alcohol and placed in the ultrasonic bath for another 10 minutes. After this process, the substrates were cleaned with deionized water and stored to be placed in the sputtering chamber. This process attempted at minimizing any residue that may provide improper adhesion of the film to the substrate [77].

Multimode optical fibers (MMF) of 600 μm core diameter were also used. Both the fiber coating and cladding were removed mechanically, leaving a section of the core exposed. This section was then cleaned thoroughly with acetone, which dissolves any leftover residue from the cladding, ensuring good film adhesion. The MMF was then cleaned with isopropyl alcohol and deionized water, in a procedures similar to the planar substrates.

Deposition of thin films varies accordingly with the material's properties, especially when comparing metals with dielectrics. For both cases, the base pressure was set at approximately 8×10^{-7} mbar, which was achieved after heating the chamber for approximately 2 hours to decrease the adsorbed gas by the chamber's walls. After this process, pressure was increased to 8×10^{-3} by injecting pure Ar (Linde Gas Portugal, purity above 99.999%), allowing the creation of plasma.

Deposition of metals was done at a rate of approximately 1.5 $\text{\AA}/\text{s}$, corresponding to 13W in Silver, 17W in Gold and 30W in Copper and Aluminium. In the case of dielectrics where deposition is considerably slower, a rate between 0.6 and 1 $\text{\AA}/\text{s}$ (depending on the material) was achieved at high power (110W).

3.2 Experimental Setup for Electromagnetic Surface Wave Excitation

As mentioned in Chapter 2, SPPs and BSWs display higher wavevectors than those supported by light propagating directly in the dielectric, meaning that to excite an ESW at a metal-dielectric or PhC-dielectric interface, a prism or waveguide of RI greater than that of the dielectric is needed. In this work two methods of ESW excitation were used, the Kretschmann configuration (which couples light using a prism) [20] and multimode optical fibers. This section describes briefly the setups developed for observation of the ESWs and their sensitivity to variations of the external RI.

3.2.1 Planar substrates

Given that the objective is to develop optical sensors for chemical and biological applications, which generally detect agents dissolved in water, a prism of RI above 1.333 (RI of water at 589nm) is needed. Thus, a prism composed of Silica glass (SiO_2) was used in the Kretschmann configuration. Figure 3.6 illustrates the experimental setup for ESW excitation in planar substrates.

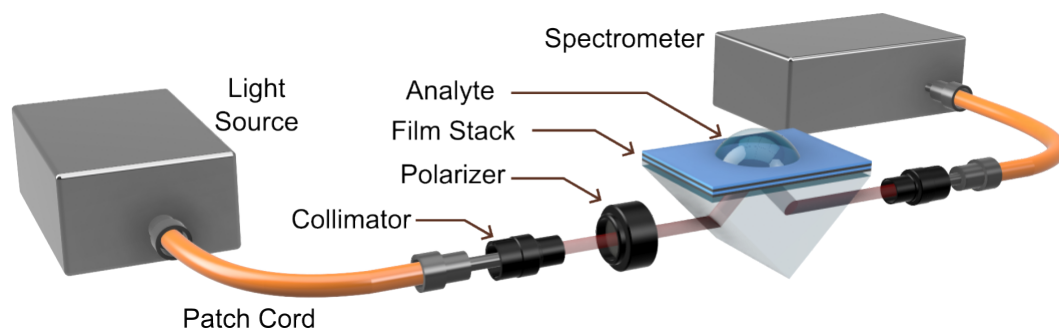


Figure 3.6: Illustration of the experimental setup for the excitation of ESWs in planar substrates.

The setup presented in Figure 3.6 couples light to the thin film structure via total internal reflection. The light is injected from a broadband Tungsten-Halogen light source (Sarspec LS-W) into the prism by a fiber optics patch cord and a collimator (Avantes COL-UV/VIS), which makes light rays travel approximately parallel. A polarizer (Thorlabs LPNIR050-MP2, working range from 650 to 2000nm) is included in front of the collimator, allowing polarization rotation. The thin films were deposited on SiO_2 substrates and placed on top of the prism using an index matching liquid which virtually eliminates the reflection losses associated with the SiO_2 -air- SiO_2 interfaces, making the substrate an extension of the prism. Light travels inside the SiO_2 prism (Edmund Optics TECHSPEC UV Fused Silica Right Angle Prisms, 25x25mm) and is totally reflected at the interface between the substrate and the external dielectric. The light reflected is then collected by a collimator into an optical fiber connected to a spectrometer. Two spectrometers were used - Avantes AvaSpec-ULS2048CL-EVO for 300 to 1100nm and Ocean Optics NIRQuest from 900 to 1700nm). In the case where the spectrometers were used simultaneously, a bifurcated fiber bundle was used.

The setup was 3D printed and designed to fit an optical table. This 3D printed piece holds the collimators, polarizer and prism and allows the placement of specially designed lid that allow changing of the analyte either manually or by integrating in a fluidic system. This design allows simple reproduction of the experimental setup and integrates with future extensions to support multiple devices at the same time. The incidence angle was set at 74° , which was chosen because it lies in the region where BSWs still demonstrate considerable sensitivity although in a more stable regime [78]. For setups near critical angle incidence (68° for an SiO_2 prism) 3D printed components may be unsuitable due to imprecisions and significant band broadening may happen with imperfect collimation. At the same time, 74° corresponds to incidence in the prism from a

horizontal position, making fabrication of the setup considerably easier. Figure 3.7 shows this experimental setup installed in an optical table.

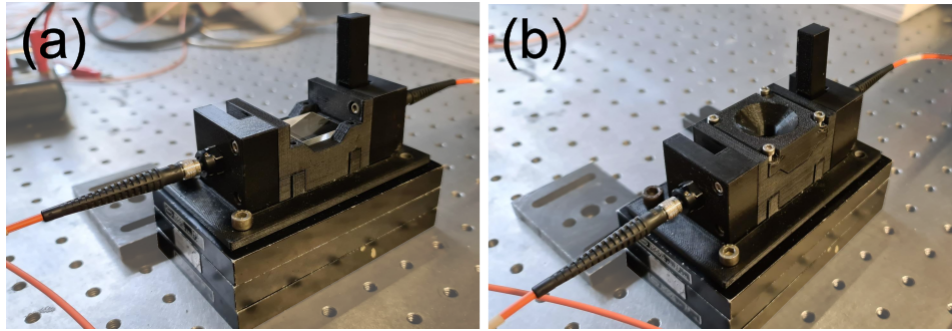


Figure 3.7: 3D printed experimental setup for the excitation of ESWs in planar substrates: (a) View of the setup with prism inside; (b) Setup with the lid on top of the prism.

From Figure 3.7 the 3D printed setup can be seen. The lid placed on top of the prism allows for manual exchange of the top analyte, this providing the necessary refractive index variations for sensitivity analysis. It presses against the substrate placed on top of the prism with an O-ring, ensuring no analyte escapes the interaction area. It can also be seen that a polarizer handle was 3D printed, allowing polarization rotation for collection of both *s* and *p* polarized spectra.

3.2.2 Multimode Optical Fibers

The second type of substrate used are MMFs with $600\ \mu\text{m}$ core diameter. As mentioned previously, a section of these fibers was stripped of coating and cladding, allowing deposition of thin films directly in contact with the fiber core, where the light propagates. In this case, the MMF modes have penetration outside of the core and will interact with the film, exciting the ESWs. Figure 3.8 illustrates the configuration used for ESW excitation in optical fibers.

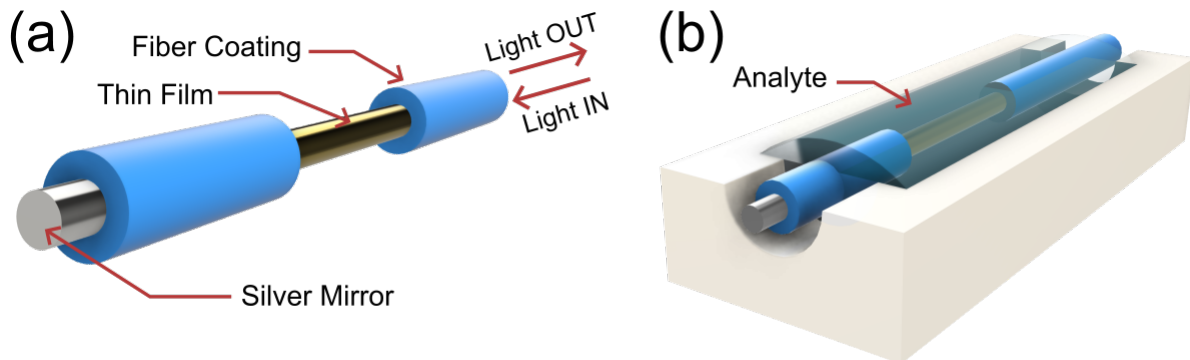


Figure 3.8: Excitation of ESWs in MMFs: (a) Configuration used for excitation; (b) Experimental setup for refractometric sensitivity testing.

As can be seen in Figure 3.8 (a), the coating and cladding of the optical fiber was removed

in two regions, one containing the thin film coating for SPP or BSW excitation and another with a silver mirror. In this case, light is coupled into the fiber by a light source connected with a bifurcated fiber bundle. Light enters the fiber and interacts with the thin film, exciting ESWs. Then, light suffers reflection at the silver mirror and interacts again with the thin film. Through the fiber bundle, light is collected by the spectrometer, producing reflection spectra and registering the ESW band. Silver was chosen for the mirror due to the high reflectivity and availability. This mirror was then coated with CeysTM Araldite Glue for mechanical and oxidation protection.

Determination of the sensitivity of the deposited MMF was made by placing the fiber in a U-groove Teflon piece, as illustrated in Figure 3.8 (b). Several analytes of different RI were placed in contact with the fiber, and the spectra were taken using the spectrometer's software.

3.2.3 Refractive Index Solutions

The presented experimental setup allows the collection of reflection spectra associated with the deposited multilayer structures. In order to test the sensitivity of the different modes to variations of the RI of the external dielectric, several solutions of calibrated RI were placed on top of the devices, as illustrated in Figures 3.6 and 3.8. These solutions were fabricated by dissolving sucrose in deionized water in different ratios, and their RI was measured using an Abbe refractometer (Atago DR-A1, measurements made at 589nm). Solutions ranging from 1.333 to 1.385 RIU were fabricated using this technique.

3.3 Simulation Procedure - Transfer Matrix Method

3.3.1 Computational Implementation

Design and optimization of optical devices requires the combination of both simulation and experimental work. In the design of 1D structures that support ESWs, the Transfer Matrix Method (TMM) presented in Section 2.1 was employed, allowing the simulation of the optical response of any 1D structure composed of stacks of isotropic materials.

In order to fully take advantage of the TMM formalism, a home-made Python based code was developed, which allows full calculation of the optical properties of 1D stacks. The code was optimized by adding compilation with Numba [166], which allows just-in-time optimization to display performances similar as C, C++ and Fortran. This optimization is of great importance in simulations of optical fibers, where integration of the reflection spectra over a large range of angles is performed.

While similar TMM based software was available in both Python [167, 168, 169] and other programming languages [170, 171], no complete package was found that performed all three needed tasks: calculation of reflection spectra, calculation of electric or magnetic field components

and calculation of the dispersion relation of multilayer structures. Relying on the formalism presented previously, the implementation of the three referred tasks is here briefly presented.

Calculation of Reflection and Absorbance Spectra

In the experimental setup devised, the reflectance or absorbance spectrum of an optical structure is measured by a spectrometer after having light incident in the substrate through a prism. In the case of reflectance, the percentage of power associated with a wavelength interval (the resolution of the spectrometer) as function of the wavelength is presented. This measurement needs a reference, which generally is taken as the spectrum of light reflected off a substrate without film. On the other hand, absorbance A as a function of the wavelength λ is defined as [125]

$$A(\lambda) = 10 \log_{10} \frac{I_0}{I(\lambda)} \quad (3.1)$$

where I_0 is a reference intensity used for normalization and $I(\lambda)$ is the measured spectrum.

Calculation of reflectance using the TMM formalism requires the construction of the transfer matrix $\mathbf{M}$ of the system, which is done by implementing Equation 2.14 computationally. Thus, the program loops over every interface and layer and performs matrix multiplications of the interface and propagation matrices to construct $\mathbf{M}$. Then, the reflectance spectrum is calculated by using Equation 2.20. This process is done for a range of selected wavelengths, thus producing a complete reflection spectrum.

The calculation of the absorbance spectrum uses the reflectance spectra as a way of determining the ratio I_0/I in Equation 3.1. In optical devices designed for biosensing, the measurements are generally made in an aqueous environment (where specific molecules or agents for detection are present). As such, the reference intensity is generally taken before placing the device in water. In the simulations, this is done by calculating the reflection spectrum in the air (R_1) and in the water (R_{H_2O}), and the ratio is calculated due to the fact that $I_0/I = R_1/R_{H_2O}$.

Calculation of the Fields Inside a Multilayer Stack

Determining the fields inside a multilayer structure is one of the most important steps in optical device design due to the fact that this process allows a better understanding of where light has the largest amplification. In the case of optical sensors, designing structures that have maximum amplification at the interface is of the utmost importance.

In the software developed, the tangential component of the electric (s polarization) or magnetic (p polarization) fields is calculated, which fully determines the field configurations. This calculation is done by using the fact that inside each layer the field is given by a sum of forward and backwards propagating waves [121], with coefficients Ψ_n^+ and Ψ_n^- (Equation 2.14),

respectively. Thus, field calculation requires only the determination of these coefficients at every position inside the multilayer structure.

The software considers an incident plane wave ($\Psi_0^+ = 1$ and $\Psi_0^- = 0$), and the position inside the structure is discretized. Taking the multilayer configuration (materials and thicknesses) and the properties of light (frequency and wavevector), the matrix $\mathbf{M}$ is calculated at every position and the field amplitudes are determined. Thus, the tangential component of the fields can be determined in this position resolved algorithm, providing crucial information for optical device design.

Calculation of Dispersion Relations

As seen in Chapter 2, one of the most important tools in analysing an optical device is its dispersion relation, which gives the relation between the frequency and wavelength of the modes. The dispersion relation is a useful tool that allows the study of the modes supported by the device and, in case of devices excited in the Kretschmann configuration, the response given by light incident with different angles or prisms of different materials.

Calculation of the dispersion relation starts by establishing a grid in the ω, k_x space by discretizing both. The software then iterates over all ω, k_x pairs using the bound state condition (Equation 2.24), and employs the bisection method to calculate this condition with precision. Figure 3.9 compares the dispersion relation of a metal slab (which supports two plasmonic modes), which can be calculated numerically using Equation 2.64 with the calculation made by employing Equation 2.24 with the same geometry and materials.

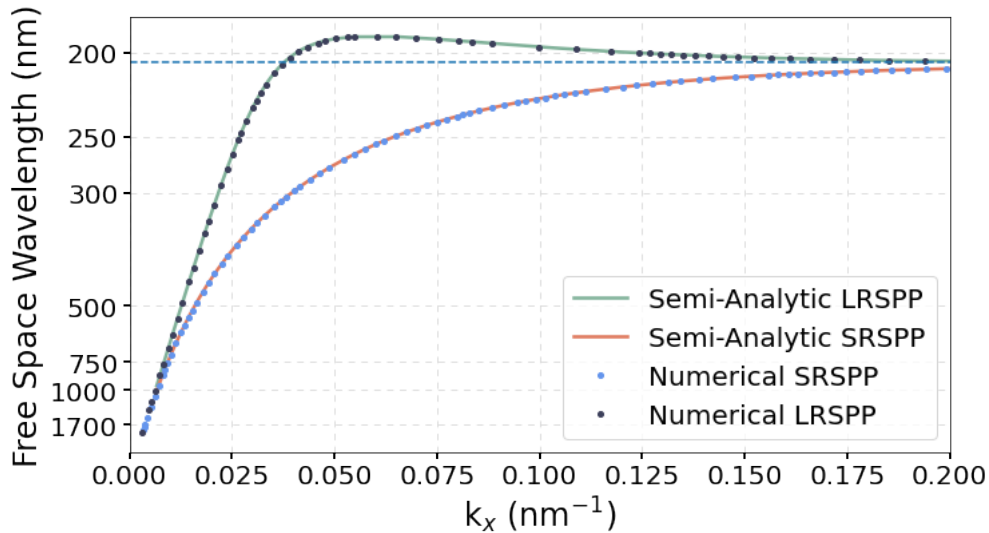


Figure 3.9: Comparison between the semi-analytical (calculated using Equation 2.64 and the numeric results obtained from the Python based TMM software).

As can be seen in Figure 3.9, excellent agreement is found between the two methods, thus

validating the approach implemented in the software. The main advantage of this implementation is the calculation of the dispersion relation of any multilayer stack, thus granting the needed flexibility for optical device design.

3.3.2 Realistic Simulation of Planar Film Stacks and Multimode Optical Fibers

3.3.2.1 Planar Substrates

As mentioned in Section 2.3, simulation of the optical response of devices must take account of the experimental details related with the way the ESWs are excited. In particular, when calculating reflection spectra, the fact that the light is injected in the system and collected through fiber optics leads to imperfect collimation because the light source (the fiber tip) is not a perfect point-like source. Figure 3.10 illustrates this process.

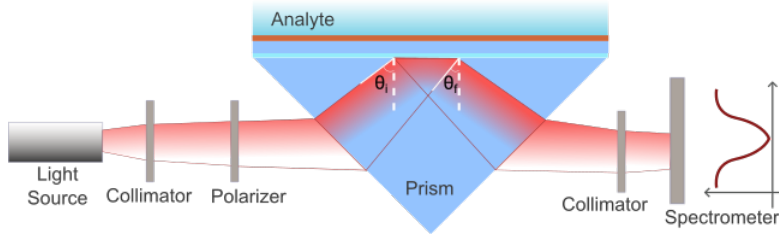


Figure 3.10: Illustration of the light injection in the prism coupling setup. Notice how the light collected to the spectrometer does not result from a single incidence angle.

Figure 3.10 illustrates how the light that reaches the spectrometer results from multiple incidence angles in the prism-film interface. In practice, these multiple incidence angles will display small shifts in the peak wavelength of each other, ultimately leading to a broadening of the ESW band. Thus, this effect must be incorporated in the simulations in order to produce realistic results.

The broadening of the spot size was measured experimentally in the fabricated setup (by measuring the spot size at injection and collection by the optical fiber) and determined to be of approximately 2° . Thus, the simulations need to account for this broadening effect caused by incidence of light rays from 73 to 75° .

Incorporation of this effect follows closely the manner in which MMFs are simulated using the TMM. The power reflection coefficient R_{planar} will be

$$R_{planar} = \frac{\sum_{\theta_i}^{\theta_f} R(\theta)}{N} \quad (3.2)$$

where θ_i and θ_f are the inferior and superior angle bounds (73 and 75° , respectively), $R(\theta)$ is the reflectance of the structure at an incident angle θ and N is the total number of angles

considered in the discretization. This process assumes a constant distribution of power over all incident angles. In this manner, realistic simulations of optical structures can be achieved by incorporating the broadening effect into the TMM.

3.3.2.2 Multimode Optical Fibers

The TMM formalism was also extended in order to allow for simulations of MMFs. This process is only possible in fibers with very large diameters, where propagation of light can be approximated by light rays propagating in a straight line [172]. This is approximately true for fibers in which the core diameter is much larger than the wavelength considered, which is the case for a 600 μm MMF. In this case the fiber will have a continuous incidence of rays ranging from the critical angle (θ_{cr}) up to 90° . Figure 3.11 illustrates this process.

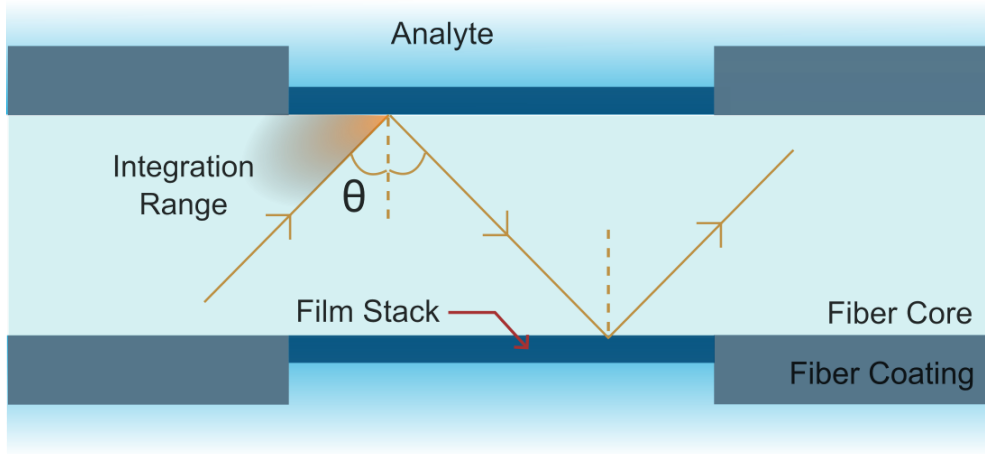


Figure 3.11: Illustration of the ray approximation of light propagation in a MMF. Multiple angles inside in the core-film interface, leading to a broadening of the ESW band.

In Figure 3.11, it is possible to observe that not only the incidence of multiple angles has to be considered but also multiple reflections on the fiber-film interface must be accounted for. From simple geometric considerations it can be seen that the number of reflections at the core-film interface is given by $N(\theta) = L/(D \tan \theta)$, where L is the length of the film section and D is the fiber core diameter. Under these assumptions, the power transmission coefficient T_{fiber} can be calculated as [173]:

$$T_{fiber} = \frac{\int_{\theta_{cr}}^{\pi/2} R^{N(\theta)}(\theta) P(\theta) d\theta}{\int_{\theta_{cr}}^{\pi/2} P(\theta) d\theta} \quad (3.3)$$

In Equation 3.3, an angular distribution of the optical power $P(\theta)$ is included to weigh in the different distribution of optical power in the fiber along rays of different angles. This factor is used in the normalization of T_{fiber} . Gupta et al. use a specific distribution associated with

coupling light to the fiber using a collimator and a microscope lens [173]. In the experimental setup developed, no lens is used, and the angular distribution follows a gaussian profile with maximum at $\pi/2$ (parallel to the fiber) and a standard deviation of 6° [174, 175]. Notice also that the multiple reflections are accounted for by performing in the power exponent of the reflection coefficient.

The implementation of Equation 3.3 in the software is similar to the one presented in Equation 3.2, where the integration is discretized over the range of angles, with the integral converting to a summation in the limit where the angle spacing is minute.

Chapter 4

Experimental and Simulation Results

In this chapter the experimental and simulation results are presented. Firstly, basic studies on the the excitation of SPPs and BSWs are reported, which correspond to the first experimental results obtained. These studies allowed a first validation of the experimental setup and basic characterization of the ESW's sensitivities. The excitation of SPPs and BSWs was tested in both planar substrates and MMFs, allowing also integration in other lines of work within the research group.

After these first observation results, two different studies are presented. The refractometric sensitivity of BSWs is firstly investigated, presenting the comparison between the TMM simulations, the perturbation theory approach explained in Chapter 2 and the experimental results. Then, a study on the simultaneous excitation of BSWs and SPPs in MDPhCs is also presented and discussed.

4.1 Characterization of Electromagnetic Surface Waves

4.1.1 Surface Plasmon Polaritons

Planar Substrate

One of the first tests to the experimental setup consisted in the deposition of different plasmonic metals and characterizing their RI sensitivity. As seen in Section 2.2, while gold is used as the standard plasmonic metal due to stability and resistance to oxidation, other metals such as silver, copper and aluminium may be used in plasmonic applications as well. Thus, in order to test both the sputtering and the ESW excitation setups, multiple tests with different materials were performed.

Firstly, a structure consisting of a 50nm gold and a 5nm chromium adhesion layer (on top of an SiO₂ substrate) was tested. Figure 4.1 plots the simulation and experimental results associated with external RI variations.

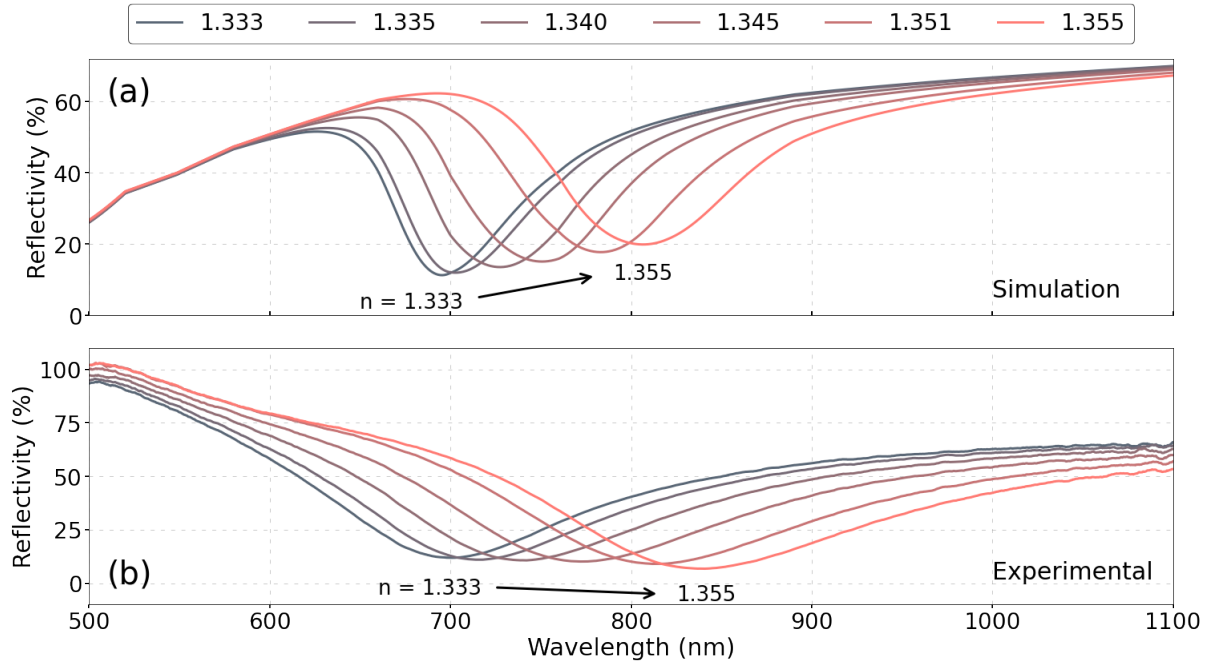


Figure 4.1: SPP bands under varying external RI for a 50nm Au film with a 5nm Cr adhesion layer: (a) Experimental results; (b) TMM simulations.

In Figure 4.1 good agreement between the experimental results and the simulations is seen for the peak position of the bands. While the large sensitivity is clear, a very high FWHM is also verified, which is larger than the simulation predictions. Further repetitions of this deposition had very similar results, implying that the explanation for the large linewidth must lie in the properties of the materials. The effect of the adhesion layer may be larger than predicted by the TMM simulations, which has been investigated in previous publications [149]. The simulations use the permittivity data obtained for thin Cr films (20 to 50nm) [176], which have very different optical properties than 5nm films. Also, due to the fact that these films were fabricated before the sputtering system optimization, the surface roughness and grain size may also significantly dampen the plasmonic response. Nevertheless, the results in Figure 4.1 confirm the excitation of an Au plasmon, which serves as a comparison standard for plasmonic modes of other materials.

Figure 4.2 presents the simulation and experimental results for a 50nm Ag film protected by a 15nm SiO₂ layer on top. The dielectric material on top protects the Ag layer from oxidation.

Similarly to the Au case, good agreement in the peak position is seen between the experimental and simulation results in Figure 4.2. Nevertheless, the opposite behaviour is seen regarding the FWHM, where the experimental band is slightly sharper than the simulation results. This disagreement is most likely due to difference in the optical properties of Ag used in the simulations and the deposited film. In the simulations the optical properties used were measured by Johnson and Christy [177] using thermal evaporated films. In silver films the quality of deposition is extremely important due to the influence of grain size and cristallinity on the conductivity of the layers, which directly influence the SPP [178]. In general, sputtering deposition of the Ag layers

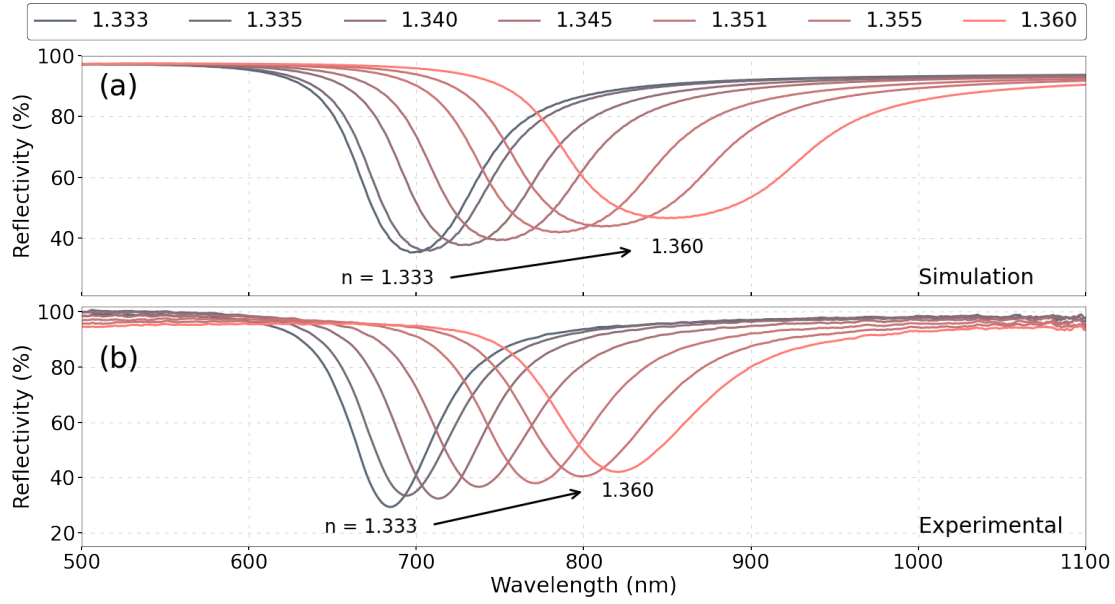


Figure 4.2: SPP bands under varying external RI for a 50nm Ag film covered by a 15nm SiO₂ layer: (a) Experimental results; (b) TMM simulations.

produces films of higher quality than thermal evaporation, explaining the sharper resonance seen in Figure 4.2.

Comparing Figure 4.2 with 4.1 it can be seen that the Ag film produces SPP modes which are much sharper and almost as sensitive. This higher quality of the plasmon can be traced to the higher conductivity of the silver films (which is directly associated with the DL loss parameter γ), which reduces the scattering of the coherent electronic motion associated with the SPP mode, reducing the FWHM considerably.

The effect of the cap layer placed on top of the Ag film is of great importance to SPP based sensors. This layer not only protects the metal layer from oxidation but also changes the SPP dispersion, making it tend to a value of $\omega_s = \omega_p / \sqrt{1 + n_d^2}$, where n_d is the dielectric's RI. This effect shifts the SPP curve to higher wavevectors and higher wavelengths, increasing the RI sensitivity. A cap layer of silicon ($n_d = 3.93$ at 589nm) was chosen due to its extremely high RI. Thus, a structure composed of a 50nm Ag film, 15nm Si and 5nm SiO₂ was deposited. The last layer protects both Ag and Si from oxidation. The thickness of the Si layer was chosen to place the SPP resonance near 1100nm, where the imaginary part of the permittivity of Ag is still relatively low (it increases greatly at higher wavelengths), so a large broadening of the band isn't observed. Figure 4.3 presents the results of both simulation and experimental results of this structure.

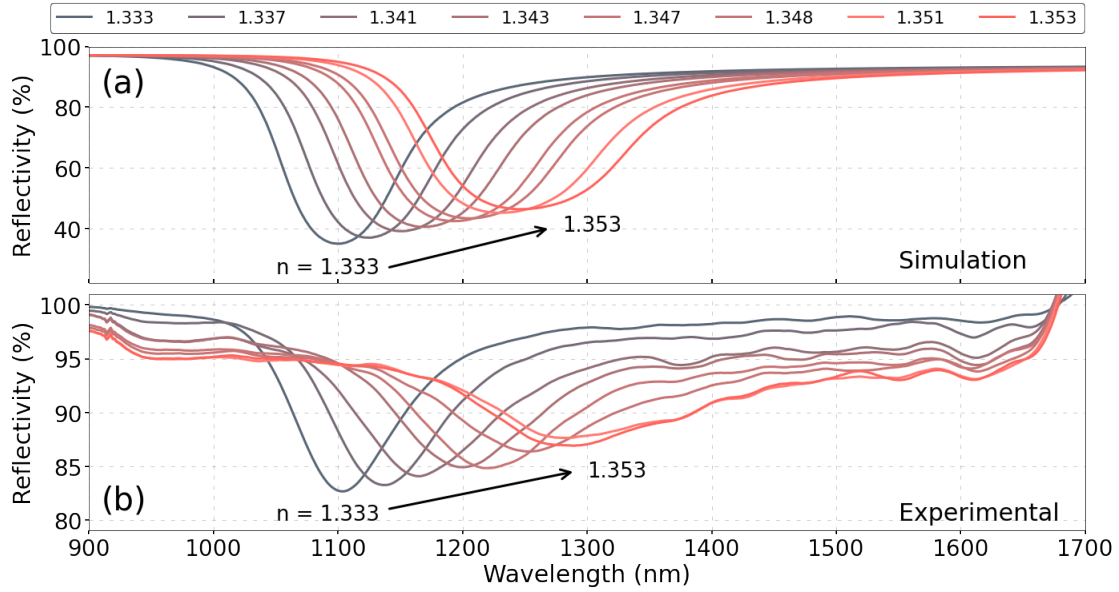


Figure 4.3: SPP bands under varying external RI for a 50nm Ag film covered by 15nm Si and 5nm SiO₂ layers: (a) Experimental results; (b) TMM simulations.

The same effect seen in Figure 4.2 is seen in Figure 4.3, where the experimental band is considerably sharper than the simulations, which is most likely due to the same effect of the Ag film. It is also seen that the experimental results have considerably less amplitude than the simulations, which could be explained by losses associated with the Si layer. Semiconductor materials behave similarly to dielectrics regarding the optical properties but show higher losses, especially for wavelengths in the visible range (although in the infrared some losses may still be present) [125]. Nevertheless, as will be seen, this structure not only protects the Ag layer but displays extremely high sensitivity while maintaining a sharp resonance, which are ideal conditions for an optical sensor.

Figure 4.4 presents the simulation and experimental results for a 45nm Cu film protected by a 15nm SiO₂ layer on top. Similarly to the Ag case, the dielectric material protects the Cu layer from oxidation.

Very similar results to the gold SPP are seen, although a wider resonance is observed. This broadening effect is in agreement with the higher DL loss parameter γ seen in Table 2.1. This implies that the imaginary part of the metal's permittivity is higher, which is associated with higher optical losses and greater damping of the SPP. It should be noted that sputtering deposition of Cu films requires a low base pressure and very clean atmosphere to reduce influence of O₂ in the oxidation of the metals [163]. Only after the sputtering chamber improvements reported in Section 3.1.3 was the observation of a Cu plasmon possible.

Figure 4.5 plots the experimental and simulation results obtained for a 40nm aluminium film. While aluminium oxidizes easily, it forms an oxide layer that protects the metal underneath, forming a stable structure [179]. In this case, no dielectric cap layer is needed.

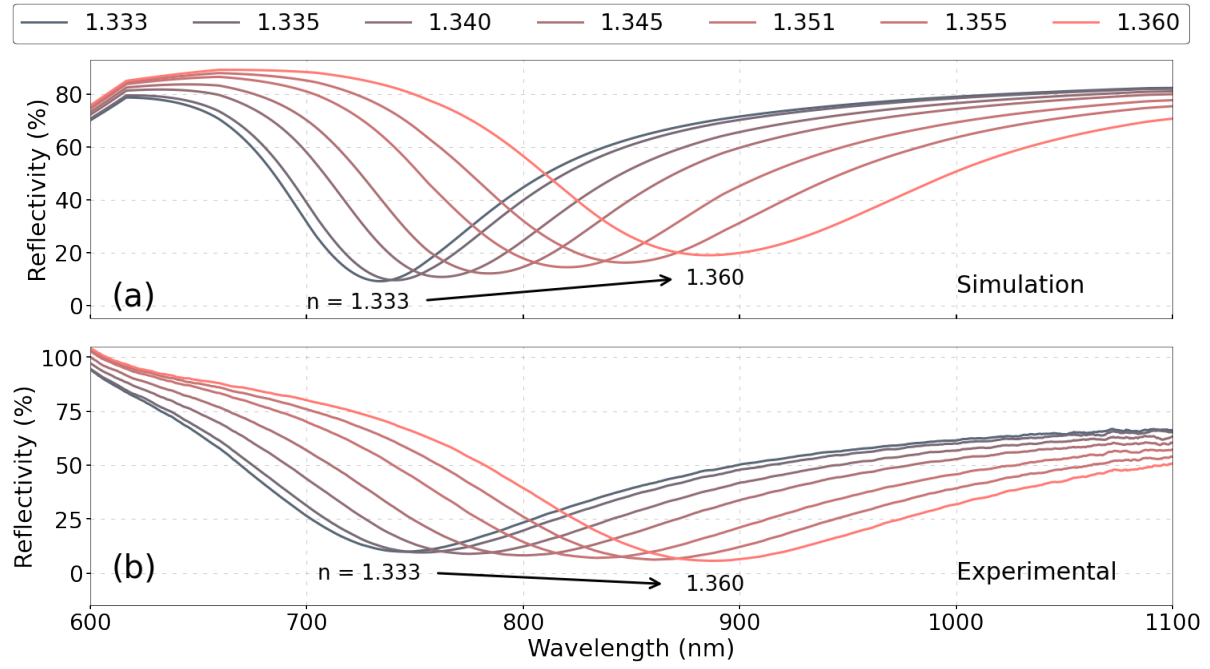


Figure 4.4: SPP bands under varying external RI for a 45nm Cu film covered by a 15nm SiO₂ layer: (a) Experimental results; (b) TMM simulations.

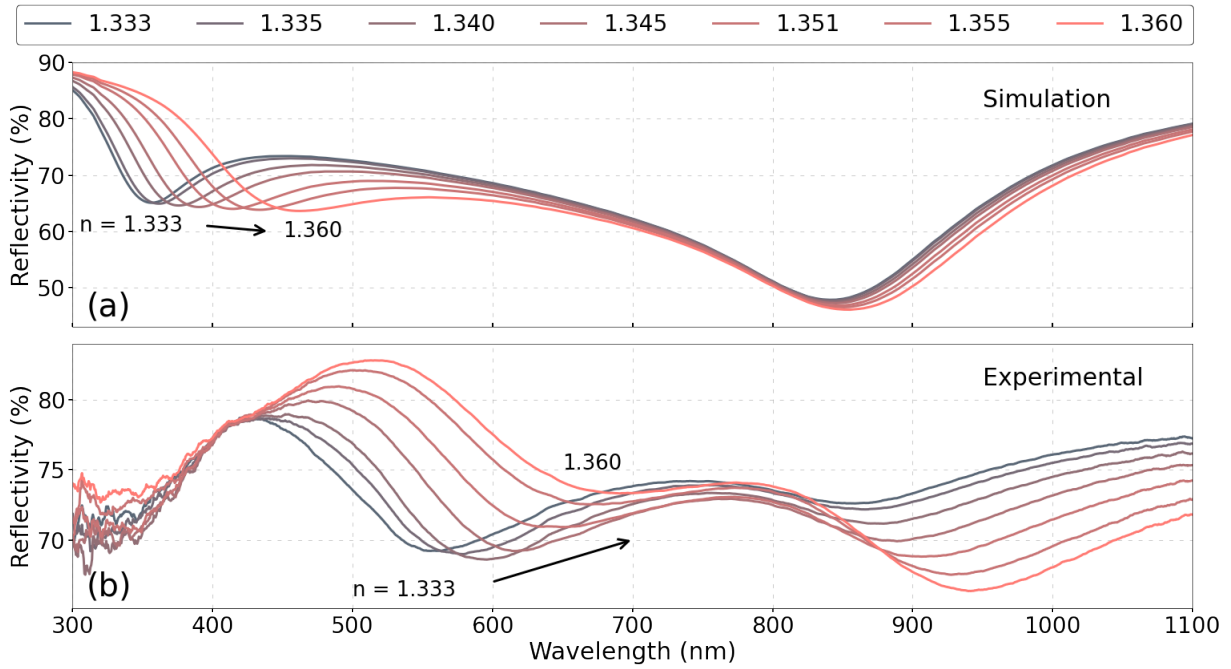


Figure 4.5: SPP bands under varying external RI for a 40nm Al film: (a) Experimental results; (b) TMM simulations.

Figure 4.5 presents some disagreement between the simulations and experimental results, in particular in the peak position of SPP mode. It can be seen that the SPP peak is considerably redshifted in comparison with the simulations. Obtaining high quality Al films by physical vapor

deposition techniques is extremely hard due to increased surface roughness [180]. As mentioned previously, increased surface roughness dampens the plasmonic response of materials, which could explain the broadening effect verified in the experimental results. Regarding the redshift observed, two mechanisms can be responsible for this effect. Firstly, an oxide layer could be forming in the surface of the metal film right after it is taken out of the sputtering chamber, which would form an effect similar to what was seen by placing Si on top of Ag in Figure 4.3, leading to a redshift of the band. At the same time, aluminium is extremely reactive in the deposition process [163], and even trace amounts of O_2 will immediately oxidise the material after it is removed from the target. A mixture of aluminium and aluminium oxide in the film could also change the optical properties of the material. Precise knowledge of the mechanism behind the redshift would require X-ray photoelectron spectroscopy and X-ray diffraction analysis, which was not possible to perform.

It is also interesting to observe the presence of a second band near 900nm. This band is a known feature of aluminium and corresponds to an interband transition of the metal, which leads to high losses in this region [125, 179]. The band seems sensitive to RI variations but this effect is most likely due to the large linewidth of the SPP influencing this region of high losses. Further study is required to understand and improve the deposition of aluminium in plasmonic applications, which is an ongoing field of research [181, 179, 182].

Given the spectra for all the analysed cases, Figure 4.6 presents the wavelength shift obtained by tracing the wavelength peak of each band.

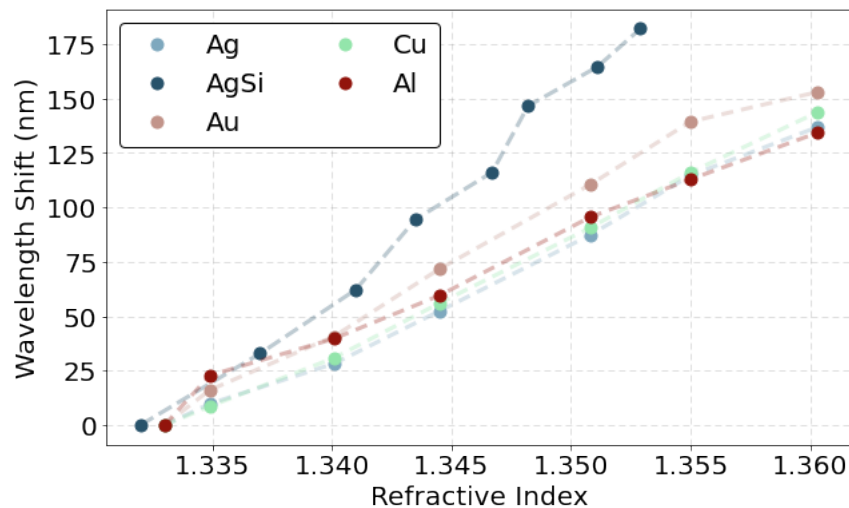


Figure 4.6: Normalized wavelength shift of the different plasmonic structures considered.

Figure 4.6 plots the wavelength shift as a function of the external RI for all plasmonic samples. It can be seen that the silver-silicon structure indeed increases the response to RI variations, with much larger shifts being observed. Regarding the other structures, gold seems to have a higher sensitivity, while silver, copper and aluminium displaying very similar responses.

By linear fitting the data presented in Figure 4.6 the RI sensitivity can be calculated. Also,

by obtaining the FWHM for each case, the FoM can be calculated. Table 4.1 summarizes the results obtained.

Table 4.1: Summary of the external RI response of the various plasmonic configurations.

Metal	Sensitivity (nm/RIU)	FWHM (nm)	FoM (RIU ⁻¹)
Au	$(5.6 \pm 0.3) \times 10^3$	274	21
Ag	$(5.0 \pm 0.2) \times 10^3$	60	84
Cu	$(5.2 \pm 0.2) \times 10^3$	232	23
Al	$(4.7 \pm 0.2) \times 10^3$	108	43.5
Ag-Si	$(9.3 \pm 0.3) \times 10^3$	92	102

From Table 4.1 it can be seen that silver is the best performing metal for sensor purposes, exhibiting a FoM considerably higher than the other plasmonic metals. This is due to its extremely sharp resonance, which compensates the lower sensitivity. On the other hand, the silicon cap layer further increases the FoM by increasing the sensitivity, while still maintaining a sharp resonance.

Regarding the other plasmonic materials, the comparison of Al with Au and Cu provides unexpected results. While aluminium losses are very high (as stated in the DL damping coefficient in Table 2.1), the resonance obtained is relatively sharp in comparison with the other two metals.

A last note should be given regarding the comparison of the results of Table 4.1 and Figures 2.13 and 2.14. It can be seen in the table that the aluminium SPP displays the lowest sensitivity and Cu shows a higher sensitivity than Ag, which is opposed to the theoretical predictions. As discussed previously, multiple factors are involved in these results. Given that the optical properties of metals are highly dependent on the deposition method and quality [163], which influence surface roughness, grain size, layer adhesion, among others, the disagreement between the theoretical and experimental results could be due to these multiple factors. Further research is needed in comparison of plasmonic metal performance in different deposition methods and under different deposition conditions.

4.1.1.1 Optical Fibers

As mentioned in Chapter 3, MMFs were also used to excite SPPs. In these fibers propagation of light can be seen as an infinite number of light rays incident on the core-metal interface at angles between θ_{crit} and $\pi/2$, leading to a large broadening of the resonance. This effect decreases the FoM considerably by increasing the FWHM, leading to sensors with worse performance than in planar substrates. Nevertheless, optical fibers display more flexibility and are easier to implement in real world situations, and much effort has been applied into optimizing their implementations.

A structure of 5nm Ti and 50nm Au was deposited on a MMF, where the Ti layer is used for better adhesion of the gold film. Figure 4.7 presents the experimental and simulation results

from the RI characterization of this fiber.

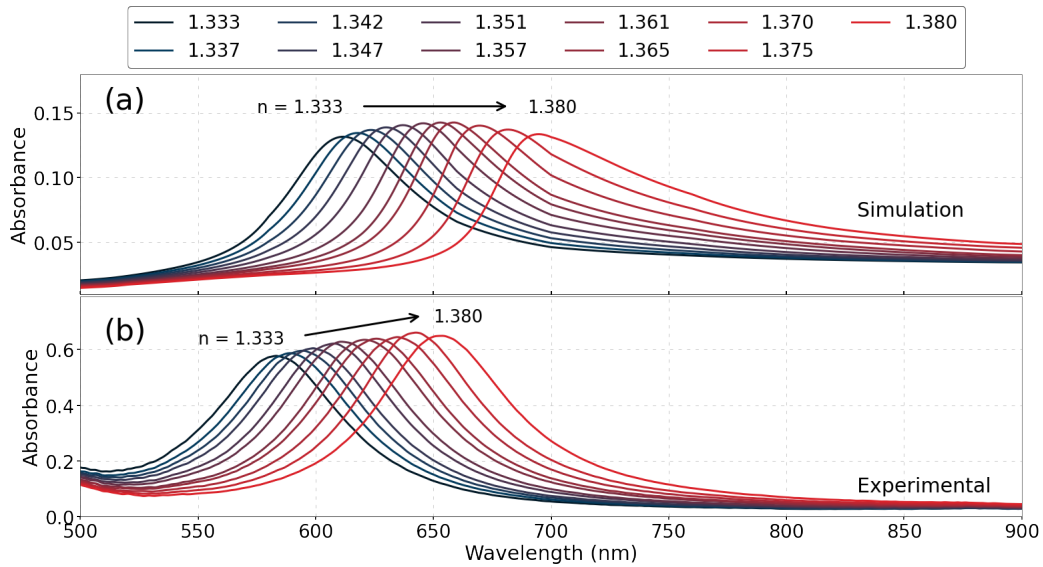


Figure 4.7: SPP bands under varying external RI for the 50nm Au covered MMF: (a) Experimental results; (b) TMM simulations.

Figure 4.7 presents the absorbance spectra (normalized to air) of the MMF for both experimental and TMM simulation results. It is interesting to observe a slight shift in the resonance peak from the simulations to the experimental results, of approximately 25nm, which can be explained by variations in the deposition conditions. Nevertheless, there is an overall good agreement between the response of the band to RI variations, with the experimental case presenting some broadening but not as pronounced as in the simulations case.

It is interesting to compare these results with Figure 4.1, which presents the same geometry but in a planar substrate. It can be seen that in the optical fiber the bands are considerably blueshifted in comparison with the planar substrate, which is the effect of the interrogation at higher angles (in an MMF most rays travel parallel to the core axis, as seen in Chapter 3). As will be seen, this effect of interrogating at higher angles also translates into a decrease of sensitivity to RI variations. At the same time, the fact that the band obtained for the optical fiber is sharper than the planar substrate is due to this blueshift, leading the mode to a wavelength where the Au losses are lower.

The gold coated fiber constitutes a standard in SPR sensing due to the fact that it is of easy fabrication and presents high chemical compatibility for surface functionalization to allow for biological agent detection. Nevertheless, as seen previously, silver presents better plasmonic properties than gold, resulting in sharper resonances which increase the FoM considerably. As such, an MMF was coated with a 50nm Ag film protected with a 15nm SiO₂ layer, also replicating a structure deposited on planar substrate. Figure 4.8 presents the experimental and simulation results for this structure.

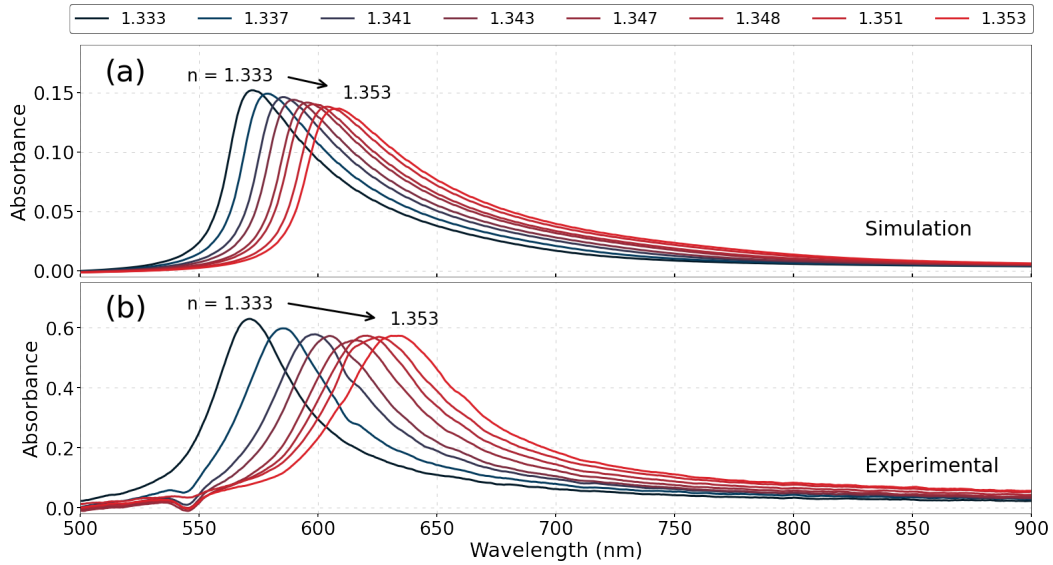


Figure 4.8: SPP bands under varying external RI for the 50nm Ag covered MMF: (a) Experimental results; (b) TMM simulations.

In the case of Figure 4.8 better agreement between the experimental and simulation results are seen regarding the initial peak position. Nevertheless, a larger wavelength shift of the band is observed experimentally, which translates into a larger experimental sensitivity. An explanation for this disagreement is not easy and requires further analysis, but it is possible that deposition conditions, which influence film quality and surface roughness are responsible for this effect.

Comparing with the MMF gold fiber, an increase in the band sharpness is seen, which is due to the lower losses associated with the optical properties of silver. As such, silver presents an excellent candidate for sensor applications, but much research is needed into developing compatibilization routines for surface functionalization. Table 4.2 summarizes the RI characterization of the two MMFs covered by plasmonic materials.

Table 4.2: Summary of the external RI response of the various MMF plasmonic configurations.

Metal	Sensitivity (nm/RIU)	FWHM (nm)	FoM (RIU ⁻¹)
Au	$(1.50 \pm 0.05) \times 10^3$	59.65	24
Ag	$(3.06 \pm 0.09) \times 10^3$	36.82	83

In Table 4.2 it can be seen that the results are in direct disagreement with the planar substrate ones, where gold was more sensitive than silver. As was seen previously, while the wavelength shift predicted in the simulations for gold was similar to that obtained experimentally, in the case of the Ag fiber the sensitivity was considerably higher.

4.1.2 Bloch Surface Waves

Planar Substrates

Similarly to the case of SPPs, preliminary tests were made to deposit a PhC in a planar substrate and test the experimental setup for the observation of BSWs. A structure composed of two unit cells (150nm TiO_2 and 140nm SiO_2) with a cap layer of 95nm of TiO_2 was fabricated. Figure 4.9 plots the dispersion relation of the PhC.

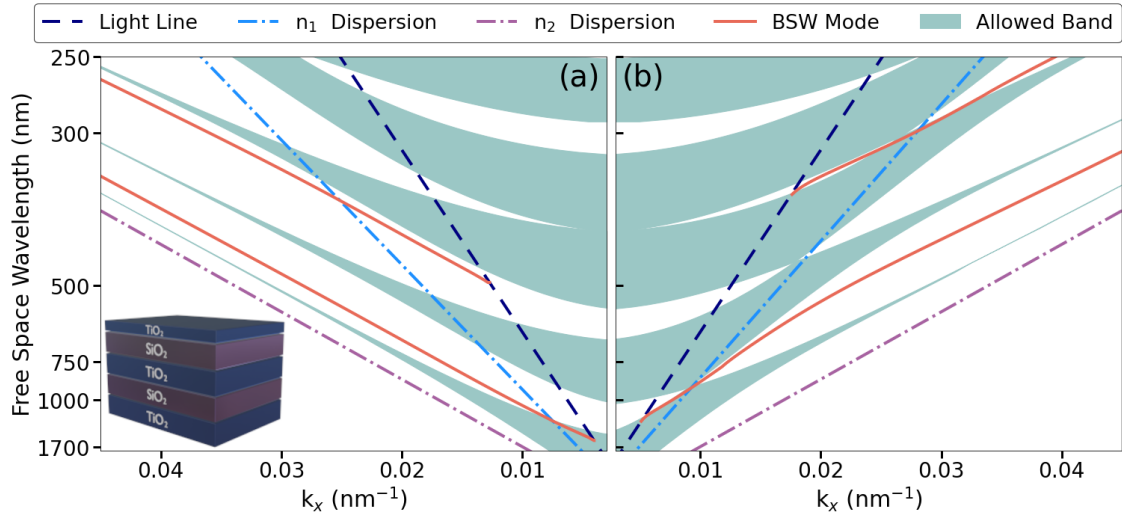


Figure 4.9: Dispersion relation of the TiO_2 - SiO_2 PhC: (a) s polarization; (b) p polarization.

As can be seen in Figure 4.9, two s polarized and one p polarized BSW modes are accessible by SiO_2 prism excitation. In the case of the s polarized modes, one lies near the UV range and another in the visible range, which will have very different RI sensitivities due to the dependence of the penetration depth on the wavelength, as studied in Section 2.3. Figure 4.10 presents the experimental and simulation results for the p polarization.

Figure 4.10 presents very good agreement between the experimental results and simulations. As studied in Section 2.3, the allowed band is composed of two different modes, which are due to the interactions of the modes originated from the two unit cells of the PhC. As expected from Figure 4.9, one BSW mode is visible in this case, which presents a much higher RI sensitivity than the guided modes. Also visible at low wavelengths is a complete bandgap, which does not possess any BSW mode.

The BSW mode observed is considerably wider and has more amplitude than expected in the TMM simulations. This may be due to surface and thickness irregularities in the PhC and the incorporation of losses in the simulations. The extinction coefficient of dielectrics is notoriously hard to measure due to its very low magnitude, and experimental values were taken from [183], which may not correspond to exact values, possibly leading to larger linewidths than in the simulation.

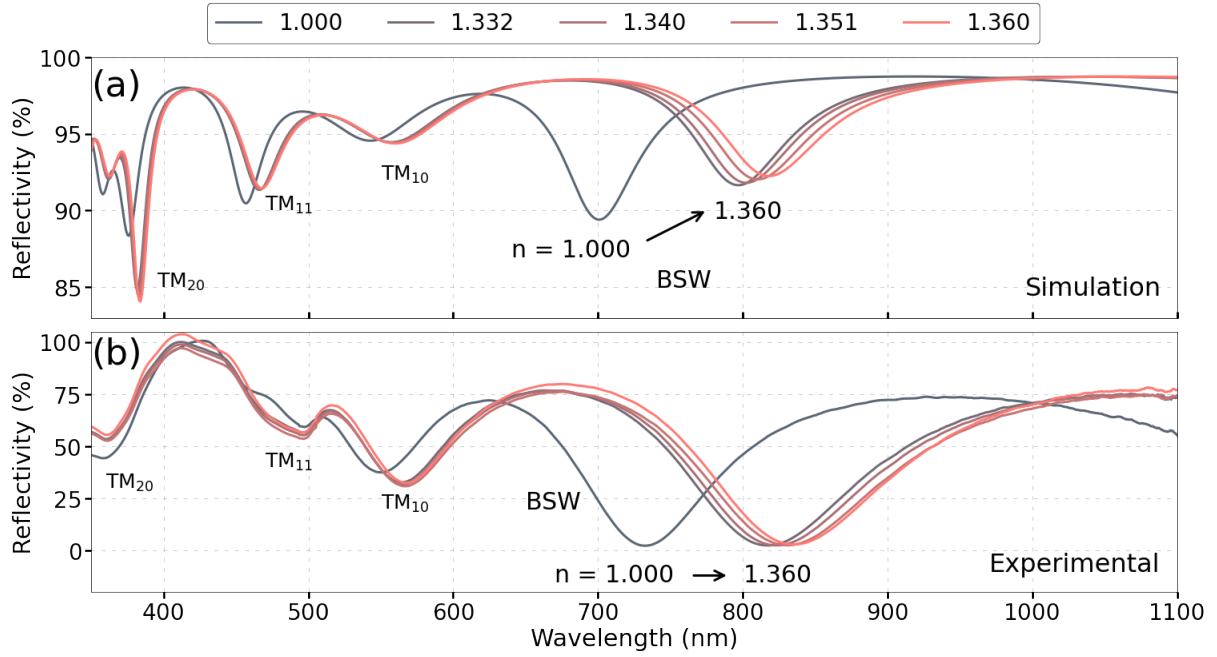


Figure 4.10: Reflection spectra of the PhC under p polarized light: (a) Experimental results; (b) TMM simulations.

Figure 4.11 presents the same analysis for the s polarization.

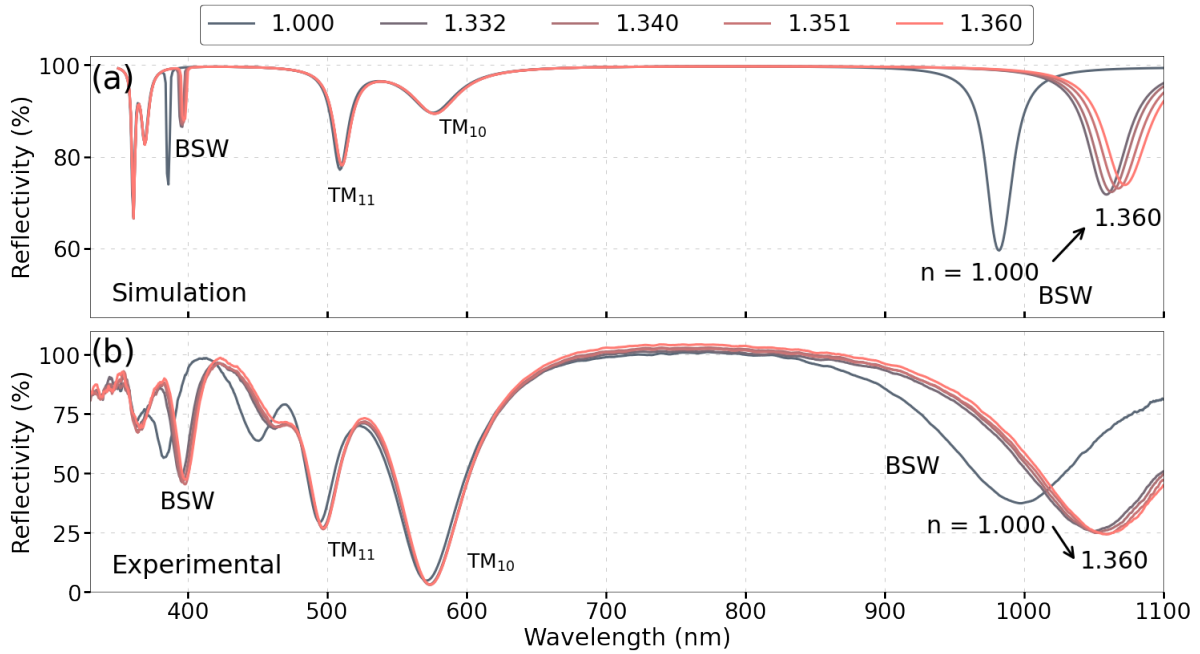


Figure 4.11: Reflection spectra of the PhC under s polarized light: (a) Experimental results; (b) TMM simulations.

Again, good agreement is seen between the experimental and simulation results, with the experimental case registering a significant broadening in the BSW modes most likely caused by

the losses in the dielectric layers. Two BSW modes are observed, one in the transition between UV and visible range (in the first bandgap, clearly visible between 380 and 500nm) and another in the near infrared.

Similarly to the SPP modes studied in Section 4.1.1, the sensitivity and FoM characterization can be performed for the BSW modes observed. Table 4.3 presents the results of the calculation of sensitivity and FoM for the proposed PhC structure.

Table 4.3: Experimental values of sensitivity, FWHM and FoM of the different BSW modes analysed in the PhC structure.

Polarization	Wavelength (nm)	Sensitivity (nm/RIU)	FWHM (nm)	FoM (RIU ⁻¹)
TM	817.5	$(6.1 \pm 0.5) \times 10^2$	103.9	6
TE	1050.0	$(4.1 \pm 0.8) \times 10^2$	124.5	3
TE	395.0	$(1.3 \pm 0.2) \times 10^2$	13.1	10

Table 4.3 shows that the the FoM of the obtained BSWs is much lower than the cases of the analysed SPPs, due both to a large increase in FWHM (for the modes in the infrared) and a decreased RI sensitivity. While the decreased sensitivity is to be expected and is related to the total amount of power associated with the mode propagating outside of the PhC, the increased FWHM was unexpected.

These results consisted of the first observation of BSWs in the research group and were obtained before the improvements made in the sputtering system, which could also explain the broadening of the bands due to surface roughness. As will be seen in the next sections, after the improvements made to the sputtering system, an excellent agreement was found between the simulations and the experimental results.

Optical Fibers

The deposition of a PhC around the core of a MMF was also tested for comparison with SPPs. The excitation of BSWs in optical fibers is a current field of research [84, 67, 83], and a preliminary test was designed. A PhC of the same thickness as the one analysed previously (2 unit cells composed of 150nm TiO₂, 140nm SiO₂, and a cap layer of 95nm) was deposited.

The deposition of optical fibers in the sputtering system requires much longer deposition times to compensate for the rotation of the fiber. Due to this factor (and previously accumulated films), the deposition took a long time and the quartz microbalance oscillated outside of the nominal frequencies, leading to large oscillations in the measured accumulated thickness. For this reason, a very large uncertainty is associated with the layer thicknesses. Figure 4.12 presents the experimental and simulation results of the RI measurements.

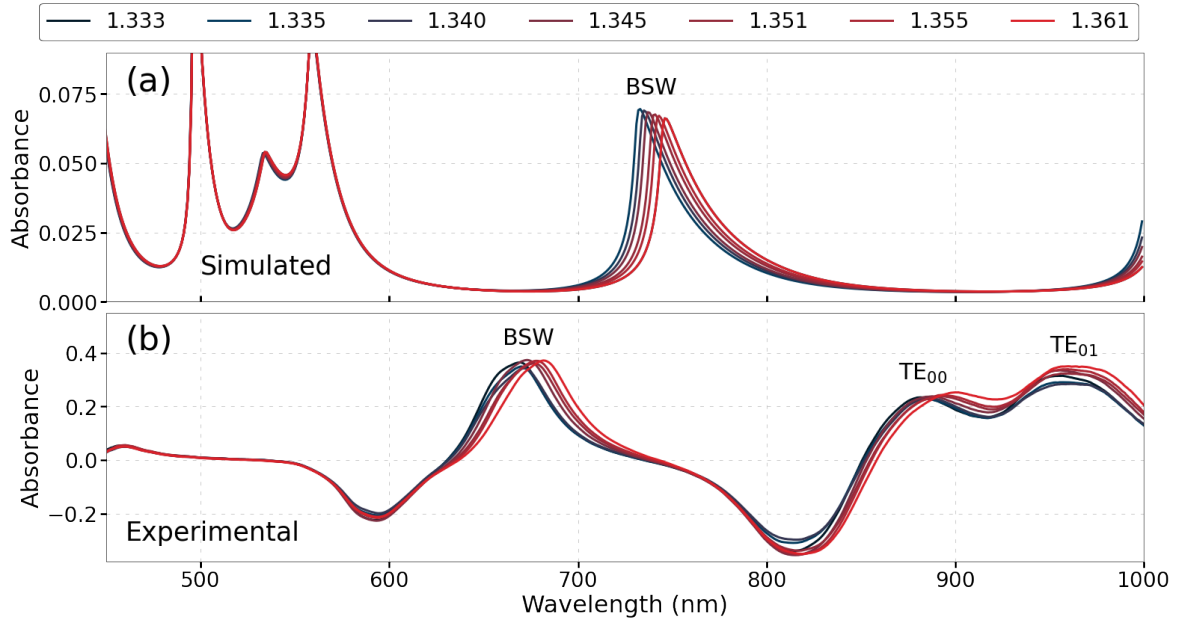


Figure 4.12: Reflection spectra of the MMF deposited with a PhC: (a) Experimental results; (b) TMM simulations.

Figure 4.12 shows the considerable disagreement seen between the simulations and experimental results, caused by the thickness uncertainty. Nevertheless, a clear BSW and two guided modes can be observed. Although a preliminary result, it corresponds to an important achievement within the research project, and further research is needed to achieve sharp resonances such as the ones seen in Figure 4.12 (b).

By analysing the experimental data collected for this fiber, a sensitivity of $(4.8 \pm 0.3) \times 10^2$ nm/RIU was calculated, along with a FWHM of 41.1 nm, giving a FoM of 12. While being considerably inferior to the FoM obtained for the SPP fibers due to the low sensitivity, it still represents an important preliminary result.

4.2 Sensitivity of Bloch Surface Waves for Refractometric and Affinity Sensing

As seen in Section 2.3, the refractometric and adsorption sensitivities of BSWs can be calculated by first order perturbation theory (PT), which assumes a small deviation from the external RI and calculates the response of the effective index to this perturbation. Along with the instrumental contribution (Equation 2.40), which depends on the prism and the dispersion of the ESW, a peak wavelength shift can be estimated.

The TMM simulations discussed in Section 3.3 allow for a direct calculation of the sensitivity of an ESW. By determining the reflection spectra of the chosen PhC under different external values of RI or variations of the adlayer thickness and tracking the peak position of the BSW

mode, the refractometric and adsorption sensitivities can be calculated directly, thus presenting a different approach for validation of the PT results.

A PhC structure was deposited using the RF Magnetron Sputtering technique discussed in Section 3.1. By directly measuring the refractometric sensitivity of the BSW, comparison can be established with the two previous methods, validating them with experimental evidence. In the study presented in this section, a direct comparison between the PT approach, the TMM simulations and the experimental results (for the case of the refractometric sensitivity) is made, establishing novel results for BSW sensing.

4.2.1 Photonic Crystal Design

The PhC was designed to support two BSWs in each polarization, one located in the near infrared and one in the ultraviolet-visible limit. The objective of such design is to test the PT approach in two very different regimes. As can be seen in Equation 2.61, BSW sensitivity depends largely on the penetration depth of the mode, which is directly proportional to the wavelength. Thus, by testing modes located at opposite ranges of the spectrum, a direct manipulation of the propagation length is done, with the infrared modes demonstrating sensitivities much larger than the UV ones. At the same time, such a structure can be interesting for affinity sensing applications, with the UV modes responding to binding events and the infrared modes responding to both binding and refractometric variations. Also, the development of optical sensors in the optics C-band (1530–1565 nm) is of interest due to low losses in optical fibers and integration with equipment already developed, also explaining the choice of location of the modes.

The chosen structure consists of two unit cells composed of TiO_2 and SiO_2 , with thicknesses $d_1 = 300\text{nm}$ and $d_2 = 140\text{nm}$. A cap layer of TiO_2 with $d_s = 120\text{nm}$ terminates the PhC structure, ensuring the excitation of BSWs. Figure 4.13 plots the dispersion relation of the PhC. (Inset com 3d da estrutura)

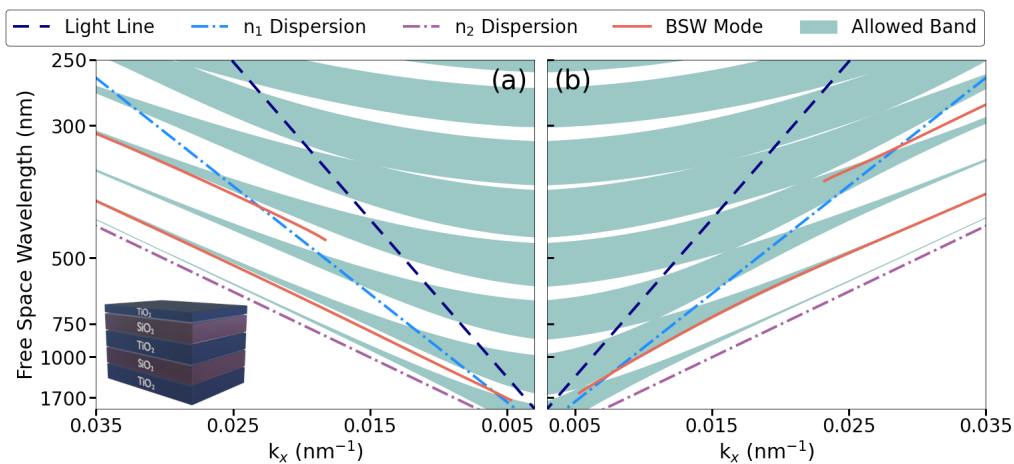


Figure 4.13: Dispersion relation of the PhC structure, for $n_{\text{SiO}_2} = 1.46$ and $n_{\text{TiO}_2} = 2.4$: (a) s polarization; (b) p polarization. Also shown as inset is the illustration of the PhC.

As can be seen in Figure 4.13, two BSW modes are present on each polarization, one propagating between the fundamental and the first band and another between higher bands (third and fourth in the TM case and fourth and fifth in the TE case). The peak associated with the reflection band is located at the intersection of the BSW mode dispersion and the prism dispersion, meaning that the modes near the fundamental band will have excitations in the near infrared (NIR) and the ones between the third and fourth bands will be in the near ultraviolet (NUV) to visible range.

The transverse fields were plotted in order to study how light propagates inside and outside of the PhC structure. Figure 4.14 presents the field configuration for the four BSW modes.

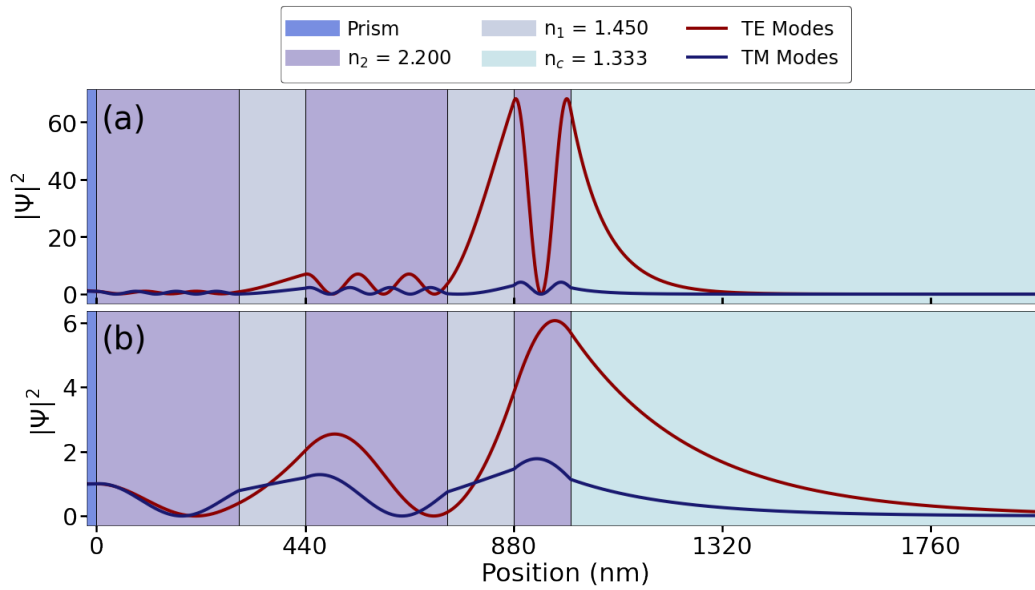


Figure 4.14: Transverse field configurations for the BSW modes, normalized at the prism-PhC interface: (a) NUV modes; (b) NIR modes.

As can be seen in Figure 4.14, the TE modes display greater magnification at the interface than the TM modes, which is an effect of the location of the mode within the bandgap [140], where modes near the band edge show less confinement. At the same time it can be seen that the penetration depth of NUV modes is considerably shorter than the NIR modes, which is explained by the dependence on the wavelength, and leads to the prediction that the NIR modes will have a larger refractometric sensitivity.

One of the most interesting observations of Figure 4.14 is the extremely large field magnification at the interface seen in the NUV TE mode, which is more than 60 times above that of the prism-PhC interface. Nevertheless, due to the excitation wavelength, the penetration depth is considerably short, explaining the fast exponential decay. This means that the field is highly confined at the interface and the mode will be extremely sensitive to variations in the interface, making it ideal for biosensing applications. The short propagation length also implies that the refractometric sensitivity will be low, meaning that the mode will be less sensitive to noise caused

by RI variations in biosensing applications.

4.2.2 Refractometric Sensitivity

Experimental Results

Figure 4.15 plots the experimental and simulation results for the s polarization, displaying both BSW modes observed.

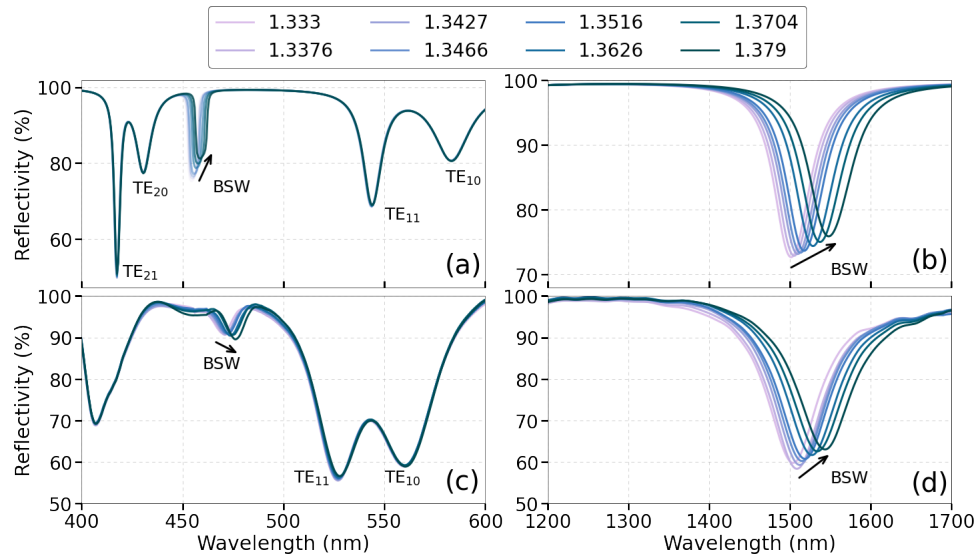


Figure 4.15: Reflectivity spectra for the PhC structure in the s polarization: (a) and (b) TMM Simulations; (c) and (d) Experimental results.

From Figure 4.15 a good agreement can be seen between simulation and experimental, with clear mode identification. As expected from analysis of Figure 4.14, the NIR mode displays a larger sensitivity to RI variations. This band is of particular relevance due to the location in the optical C-band, allowing future integration with optical fibers for sensing applications, which is a current field of research in BSWs [184, 67]. Regarding the NUV band, a small shift in the peak wavelength of the BSW mode can be seen when compared with the simulations. This effect can be caused by both a difference between the RIs of the materials used in the simulations (which may vary considerably depending on the source, especially when going near the absorption edge of the dielectric) and by slight errors in the cap layer thickness. BSWs located in the UV range display high sensitivity to the cap layer thickness (which can be explained by the high field amplification at the interface), and even small deviations in the deposited thickness may lead to relatively large shifts.

Analysis of Figure 4.15 also allows the observation that the reflectivity of the experimental results is lower than the simulations, which may be due to a larger imaginary part of the refractive index (extinction coefficient) than the simulations assume, which was obtained from [183]. The

larger extinction coefficient would lead to less pronounced bands and wider resonances, which is seen in both cases.

Figure 4.16 plots the reflection spectrum for the TM modes, also comparing simulation and experimental results.

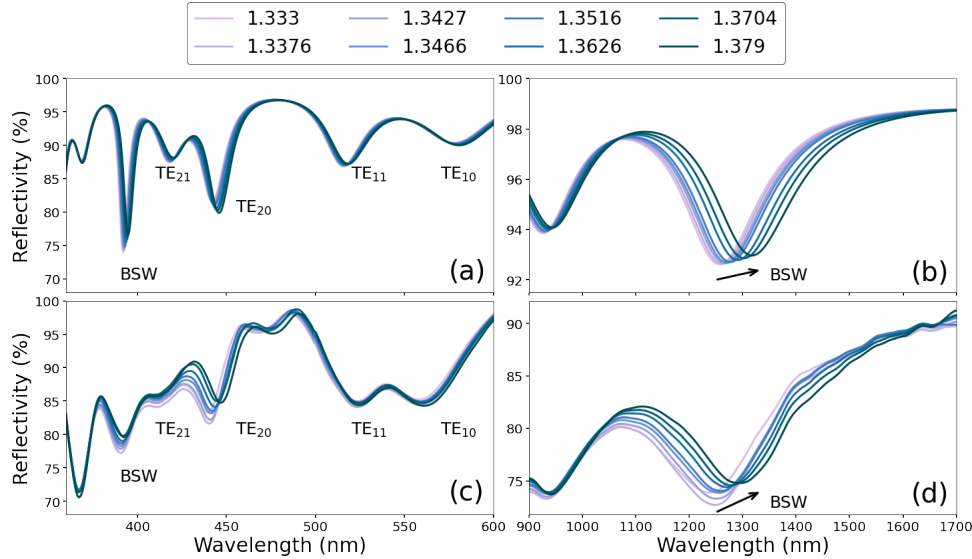


Figure 4.16: Reflectivity spectra for the PhC structure in the p polarization: (a) and (b) TMM Simulations; (c) and (d) Experimental results.

In Figure 4.16 the possible effect of the higher extinction coefficient is more noticeable than in the s polarization due to the fact that the dips in the spectra are not as pronounced, as can be seen in the simulations. At the same time, while the identification of the modes is clear in the NIR part of the spectrum, the NUV part part shows more modes, although good agreement with the simulations is observed. It should be noted that the BSW mode lies outside of the working range of the polarizer, although some degree of polarization is guaranteed by the manufacturer [185].

Similarly to the s polarization, the BSW NIR modes seen in Figure 4.16 show larger sensitivities than the NUV modes, which is to be expected as explained previously. Figure 4.17 plots the wavelength shift for all BSW modes.

In Figure 4.17 the wavelength shifts are plotted as a function of the external RI. The RS, which is defined as the derivative of the wavelength shift of the BSW modes, is calculated by performing a linear fit to the data, with the RS being the slope of the fitted line. An interesting observation is that for the TM modes the linear model only produces an acceptable fit for RI values near the normalization (RI of water), corresponding to very small perturbations. In the case of the TE modes the linear model provides an acceptable fit to the experimental results even for large perturbations. This is in direct agreement with Equation 2.61, where it can be seen that for TE modes the dependence with the external RI is linear, while for TM modes this dependence is highly non-linear. Thus, only values very near the RI of water can be used for

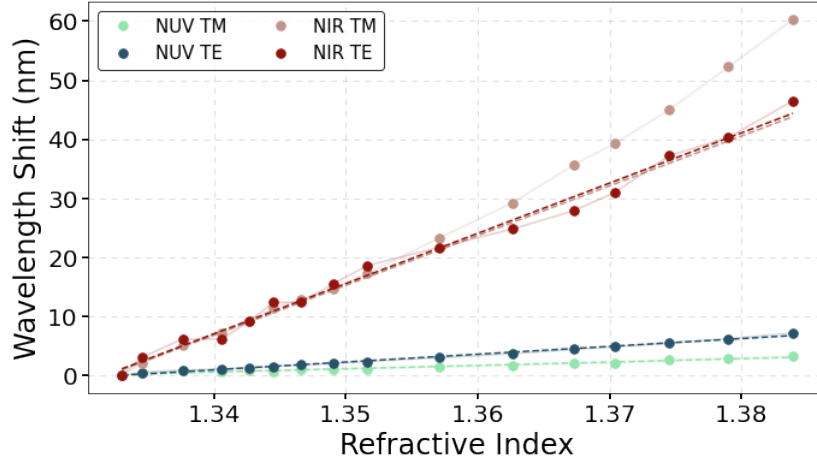


Figure 4.17: Wavelength shift (normalized to the water peak position) of the different BSW modes.

calculation of the sensitivity of TM modes with a linear model.

In the case of the UV modes, the s polarization shows a higher sensitivity, which is to be expected from Figure 4.14, where the field magnification leads to a large portion of the mode propagating outside of the PhC. Interestingly, while the NIR TE mode shows a larger penetration depth and higher amplification in Figure 4.14, Figure 4.17 shows that the NIR TM mode has a higher sensitivity. This counter intuitive result is explained by the $P/|\alpha|^2$ term in Equations 2.61, which comes from the normalization factors of the perturbation theory equations. In the case of the NIR TM mode, $P/|\alpha|^2 = 202.80$, while in the NIR TE mode $P/|\alpha|^2 = 273.00$ (calculated using the TMM simulations). This is explained by analysing Figure 4.14, the TE mode has higher magnification and propagation length but the relative amount of power that propagates outside comparing with the power that propagates inside the PhC (which is in part modelled by the $P/|\alpha|^2$ term) is inferior to the TM mode, justifying the higher sensitivity observed. Table 4.4 presents the values of sensitivity, FWHM and FoM for the BSW modes.

Table 4.4: Experimental values of sensitivity, FWHM and FoM of the different BSW modes analysed in the PhC structure.

Pol.	Peak Wavelength(nm)	Sensitivity(nm/RI)	FWHM(nm)	FoM(RIU ⁻¹)
TE	1499.83	$(8.5 \pm 0.2) \times 10^2$	73.01	12
TE	470.00	$(1.3 \pm 0.6) \times 10^2$	8.86	15
TM	1236.32	$(8.4 \pm 0.4) \times 10^2$	150.38	6
TM	389.78	$(5.3 \pm 0.5) \times 10$	21.41	3

As can be seen in Table 4.4, the TE modes outperform the TM modes, which is due to the lower FWHM values verified. Nevertheless, it is interesting to observe that the mode with the highest FoM is the TE mode in the NUV, displaying both a sharp resonance and a considerable sensitivity given the peak wavelength location.

From Figure 4.15 it can be observed that the FWHM of the modes is very stable, even when going to high RI values. Figure 4.18 plots the FWHM of the TE NIR mode.

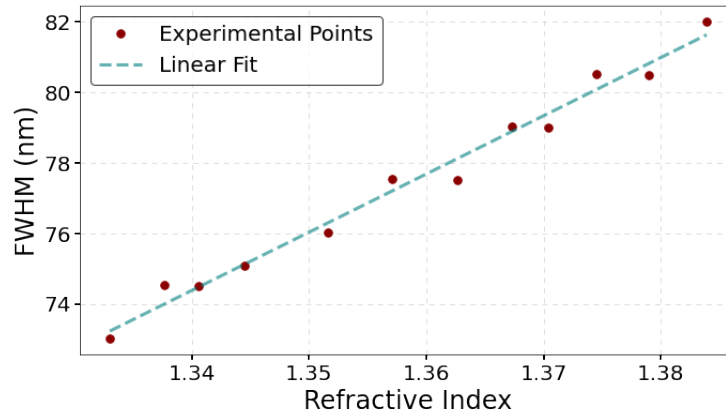


Figure 4.18: FWHM of the TE NIR mode as a function of the external RI value.

Figure 4.18 confirms the stability of the FWHM, increasing only approximately 10nm over a 0.05 RIU variation. This is an interesting feature of BSW modes which differs greatly from SPPs, where the FWHM can increase greatly even for small RI variations. In many chemical sensors the sensor is covered with a layer of a material (generally polymeric) that responds to a specific chemical agent, showing a difference in RI by detecting that agent. This RI variation shifts the BSW band, creating an optical sensor. Due to the fact that these polymers generally have high RI values (above 1.45), the layers placed on top of the SPP sensors need to be very thin (dozens to hundreds of nm), otherwise the resonance would become extremely wide or disappear. This process makes harder fabrication and sensor repeatability. Thus, the fact that BSWs can support an almost macroscopic layer of high RI materials (but always below the RI of the prism or waveguide) without considerable broadening on top can be seen as an advantage for this type of sensors.

Validation of the Perturbation Theory

Using Equations 2.61 and 2.40, the RS of the designed PhC structure can be calculated. This approach requires the calculation of the effective index of the BSW modes, which was done by numerically calculating the dispersion relation of the structure. These results can be compared with the sensitivity directly obtained from tracking the peak position of the BSW bands using the reflection spectra calculated with the TMM simulations. Figure 4.19 plots the sensitivity values obtained for the four different BSW modes present in the PhC structure considered.

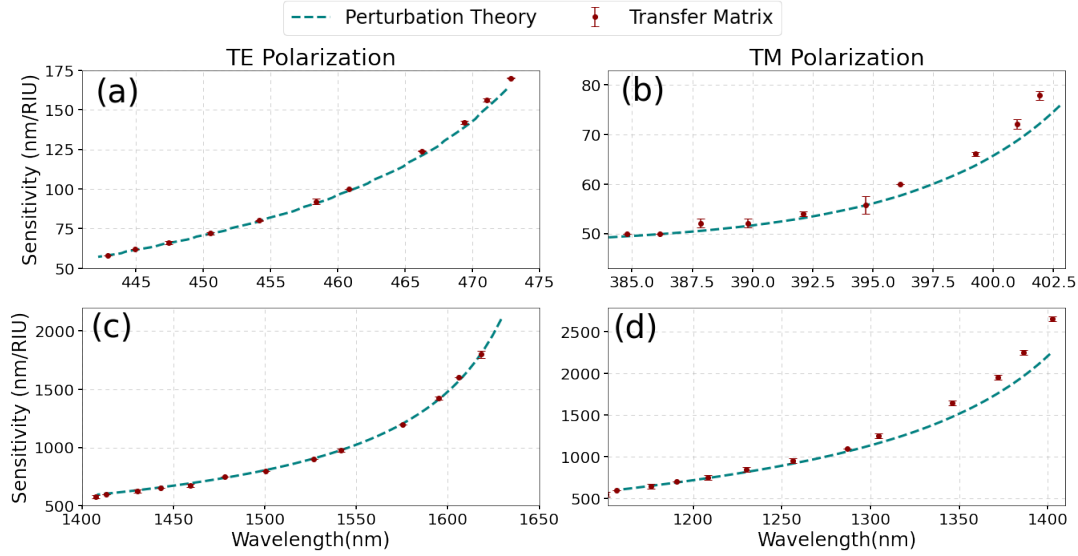


Figure 4.19: Refractometric Sensitivity of the BSW modes present in the considered PhC structure: (a) TE Mode, NUV; (b) TM mode, NUV, (c) TE mode, NIR; (d) TM mode NIR.

Figure 4.19 shows an excellent agreement between the PT and TM approaches, especially for lower wavelengths (higher values of the incidence angle and effective index), where the sensitivity is lower. As the sensitivity increases, the effect of the perturbation becomes larger and the TMM simulations differ slightly from the PT, which is especially seen in the TM modes. This slight deviation is most likely the result of the first order approximation, while the inclusion of higher order terms might lead to a better agreement. Both the PT and TMM approaches can be compared with the experimental results. Table 4.5 summarizes the sensitivities calculated from the different approaches.

Table 4.5: Comparison of the refractometric sensitivity obtained experimentally and calculated with the TMM simulations and PT approach.

Polarization	Wavelength (nm)	Transfer Matrix (nm/RIU)	Pert. Theory (nm/RIU)	Experimental (nm/RIU)
TE	1499.83	$(8.0 \pm 0.1) \times 10^2$	804.18	$(8.5 \pm 0.2) \times 10^2$
TE	470.00	$(1.5 \pm 0.1) \times 10^2$	142.53	$(1.3 \pm 0.6) \times 10^2$
TM	1236.32	$(8.7 \pm 0.3) \times 10^2$	840.14	$(8.4 \pm 0.4) \times 10^2$
TM	389.78	$(5.2 \pm 0.1) \times 10$	51.49	$(5.3 \pm 0.5) \times 10$

As can be seen in Table 4.5, excellent agreement is seen in most cases, with the experimental results agreeing with both PT and TMM approaches in both the infrared and NUV ranges, validating the TP equations obtained in Section 2.3. These equations may prove useful in future sensor design, responding to a need in the BSW sensing community of understanding the principles behind the sensitivity of BSW modes, which so far has only been done by numerical optimization or with semi-numerical approaches [186, 79, 78].

4.2.3 Adsorption Sensitivity

A similar study was made to compare the PT approach to modelling the sensitivity of a BSW when a thin layer of molecules forms an adlayer on the PhC surface. The PT results are compared with the TMM simulations. Even though the validity of this model is limited (most times the binding of a molecule to the surface does not form a uniform film) it can present a simple scheme to test the sensitivity of BSWs in biosensing.

In this case, the same structure (two unit cells composed of TiO_2 and SiO_2 , with thicknesses $d_1 = 300\text{nm}$ and $d_2 = 140\text{nm}$ and a cap layer of TiO_2 with $d_s = 120\text{nm}$) was chosen. The refractive index of the protein layer was chosen to be $n_F = 1.50$ [133], and the external RI was set to $n = 1.333$ (simulation of detection in an aqueous solution). Figure 4.20 plots the spectra obtained from the TMM simulations for the four BSW modes observed in the PhC under varying thicknesses of the adlayer.

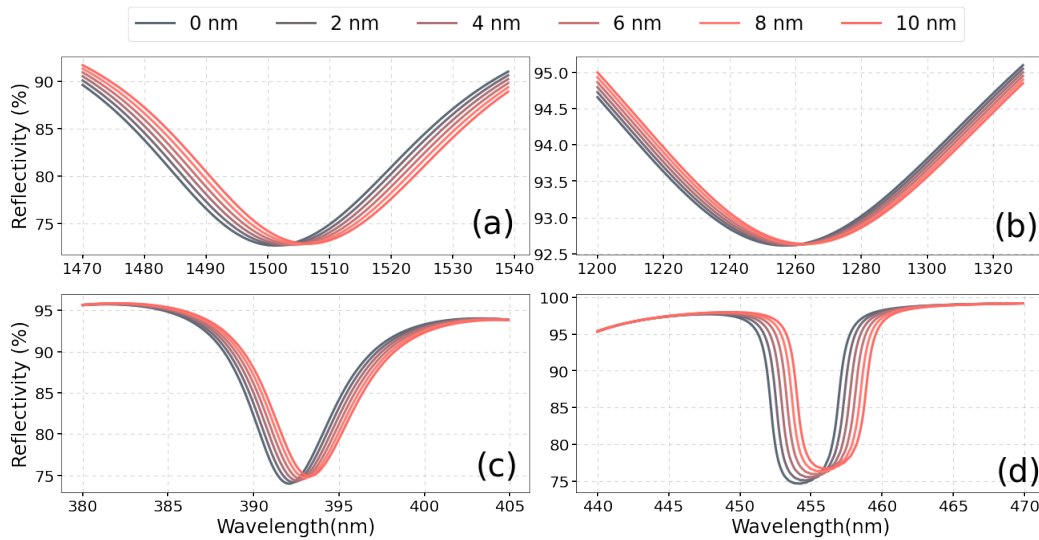


Figure 4.20: Simulated reflection spectra of the four BSW modes present in the PhC structure considered: (a) TE mode, near UV; (b) TE mode, NIR; (c) TM mode, near UV; (d) TM mode, NIR.

Figure 4.20 shows a slight redshift is observed for all modes with the increase of adlayer thickness. It can be seen that the NIR modes display a wavelength shift which is slightly higher than the NUV modes, indicating that the effect of the large penetration depth is also seen in this case. Nevertheless, the NUV modes will display lower cross sensitivity with refractometric variations in the aqueous solution, which might be an advantage.

Figure 4.21 compares the PT theory calculations for the adsorption sensitivity (using Equations 2.62 and 2.37) with the TMM sensitivity obtained from tracking the wavelength shift of the bands seen in Figure 4.20.

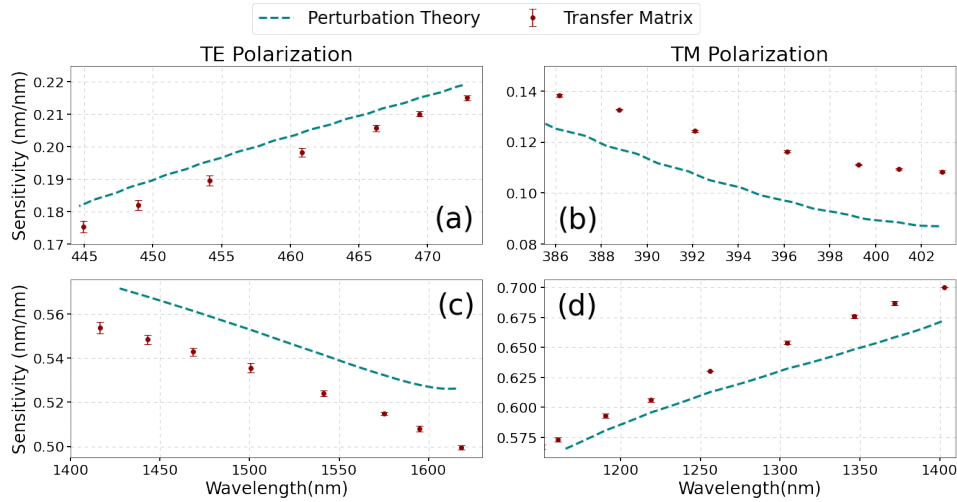


Figure 4.21: Adsorption Sensitivity of the BSW modes present in the considered PhC structure: (a) TE Mode, near UV; (b) TM mode, near UV, (c) TE mode, NIR; (d) TM mode NIR.

Figure 4.21 shows general good agreement between the two approaches for all considered modes. While the agreement seems not as good as in the case of the refractometric sensitivities, the much lower order of magnitude in the band shift should be noticed. It is interesting to observe that depending on the mode, both approaches can display the highest sensitivity at lower wavelengths (near normal incidence) or a higher wavelengths (near the critical angle). This difference may be related to a slight tuning of the position of the band with the variation of the incident angle, moving from the middle of the band gap (where the mode is more confined) to near the band edge [187, 142].

It can be concluded that the PT approach presents a fast way of calculating the adsorption sensitivity of BSWs for applications in affinity sensing. These results may provide new perspectives into PhC design for BSW sensing by providing an analytical expression for the BSW adsorption sensitivity.

4.3 Electromagnetic Surface Waves in Metal-Dielectric Photonic Crystals

As stated in Section 2.4, metal dielectric structures are an ongoing field of research, with most of the focus going into excitation of high k plasmonic modes generated in MDPHCs and HMMs. While some publications predicted that the excitation of BSWs and SPPs is possible using a PhC capped by a plasmonic metal [110, 111], the simultaneous observation of these two modes has never been reported.

In this section, the simultaneous excitation of BSWs and SPPs is reported. This observation was achieved by fabricating Ag-TiO₂ MDPHCs and recording the spectra in a large wavelength range. The devices fabricated are then characterized under external RI variations and compared

with a common plasmonic film sensor.

4.3.1 Effect of Metal Thickness in the Quality of Surface Plasmon Resonance

The study of plasmonic behaviour in thin films and multilayer stacks made in Section 2.4 assumed lossless metals, which is an acceptable approximation for noble metals such as silver and gold. Nevertheless, even in such cases, losses must be incorporated in the modelling of optical devices in order to obtain realistic responses.

While TMM simulations easily incorporate the effect of losses by including a wavelength dependent complex permittivity, the effect of thickness on the losses is not easily modelled. At low metal thicknesses, the effect of electron-grain boundary scattering becomes considerably larger [188], resulting in a large increase of the Drude damping parameter γ . This severely affects the plasmonic properties of metal films, which can be understood by the fact that electrons cannot support coherent motion due to scattering, with the SPP decaying rapidly into heat.

Several films of different thicknesses of Ag (10 to 60nm) were fabricated to test this thickness dependence on the sputtering system presented in Section 3.1. The films were deposited in SiO₂ substrates and covered with a 5nm TiO₂ cap layer for oxidation protection, and the reflection spectra at the film-water interface was obtained. Figure 4.22 plots the results of these observations.

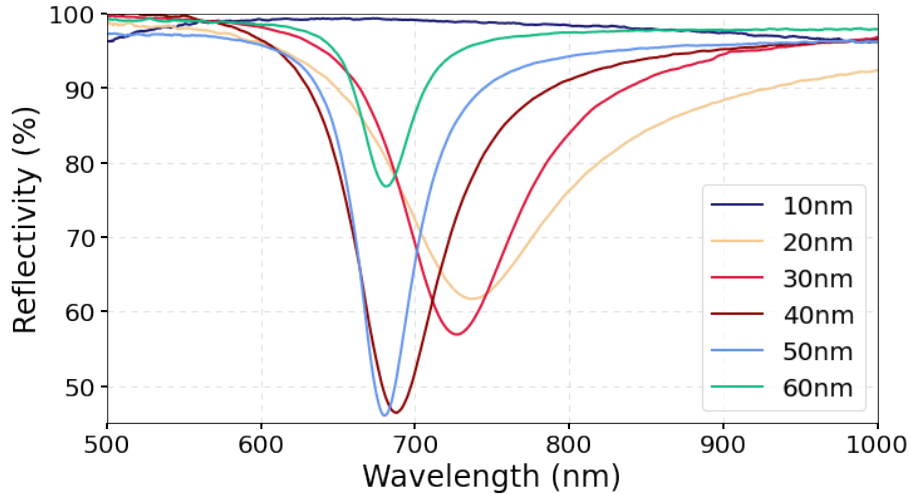


Figure 4.22: Reflection spectra of the different Ag films with an external RI of 1.333 (deionized water).

Figure 4.22 shows the thickness dependence of the reflection spectrum of the Ag SPP. As can be seen, a minimum of 20nm of film thickness is needed in order to observe the SPP, with the 10nm film showing no plasmonic mode. These results are in direct agreement with previously published works [189, 178], where a critical damping thickness of approximately 20nm was observed in silver films, below which the resistivity of the metal increases greatly and coherent

electronic motion is not possible, explaining the absence of the SPP mode at 10nm in Figure 4.22. In the range between 20 to 50nm, the plasmonic mode suffers a slight blueshift (caused both variations of Ag optical properties and by the absence of prism effects) and the linewidth decreases considerably, which is directly related with a decrease of γ caused by the lower film resistivity and optimal coupling of the SPP mode. At higher thicknesses the effect of metal losses is clear and a decrease in reflectivity is seen, although the resonance is sharper. This observation of an asymmetric SPP at low thicknesses, decreasing linewidth with larger thicknesses and reflectivity (above 50nm) is also in agreement with previous published work by Homola [48], who performed a similar study with gold films deposited on BK7 substrates.

Observation of Figure 4.22 allows the conclusion that while 50nm of Ag is the optimal thickness for a plasmonic film, thicknesses above 60-70 nm display very large light absorption, meaning that the reflection band dip associated with plasmonic modes will be hard to visualize. This effect is of particular importance in MDPHCs due to the fact that light absorption in different metal layers is cumulative. Nevertheless, Figure 4.22 indicates that for films with 20-30nm plasmonic modes will still be present and there is possibility of stacking multiple films and still have a considerable portion of light reaching the device interface.

4.3.2 Metal-Dielectric Photonic Crystal Design

A MDPHC structure was designed to allow excitation of both BSW and plasmonic modes. The structure consists of two Ag-TiO₂ unit cells, in which the top TiO₂ layer (with 30nm) is truncated and the thickness of the first TiO₂ layer (d_1) was varied. This multilayer stack was deposited on SiO₂ substrates. Figure 4.23 illustrates the chosen materials and geometry.

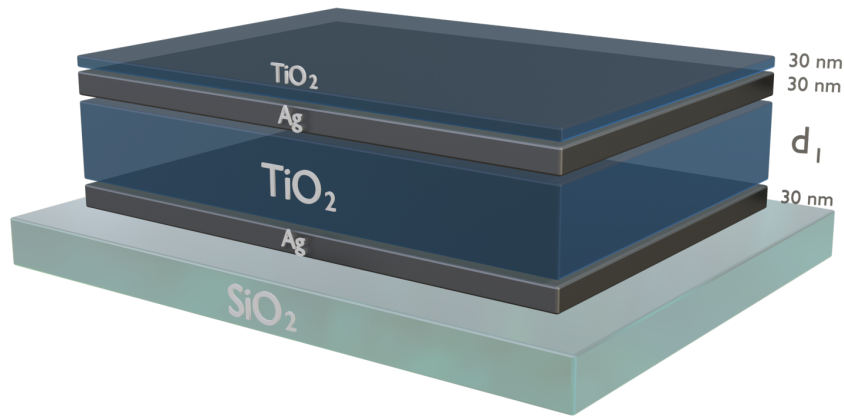


Figure 4.23: Proposed metal-dielectric structure, consisting of two Ag-TiO₂ layers with a truncated cap layer. The structure is deposited on top of an SiO₂ substrate, allowing excitation of optical modes in the Kretschmann configuration using an SiO₂ prism.

The choice of Ag as the metal in the MDPHC of Figure 4.23 is justified by its low losses, which reflect in the low imaginary part of the permittivity of the metal [190]. This choice of

metal reduces the damping that occurs in the propagating modes of the structure. The choice of TiO_2 is due to its high refractive index [191], allowing the presence of guided modes even in very thin layers. Thus, the combination of these materials aims to optimize losses and allow a clear observation of both guided and plasmonic modes.

The number of layers follows similar principles to that of the materials. Two unit cells creates a sufficient periodic modulation of the refractive index to allow an excitation of a BSW [192], while minimizing the losses induced by the metal layers. At the same time, the possibility of BSW excitation using few layers is a current research interest [67], and the proposed four layers consist of one of the fewest amounts in published literature.

The thickness of the Ag layers was set to 30nm and regards the optimization of losses associated with metal films. As seen in the previous section, for metal thicknesses above 60nm the amount of light that reaches the surface of the structure is considerably low, with the same happening for accumulation of thin metal layers. Thus, two 30nm Ag layers were chosen for this structure, ensuring that plasmonic modes can be observed and that the losses aren't too large. Regarding the thickness of the first TiO_2 layer (d_1 in Figure 4.23) values of 300, 200, 100 and 50nm were experimentally studied. This choice of thicknesses allows regimes where the structure displays guided modes on this layer in both polarizations (for $d_1 \geq 50\text{nm}$), essential for BSW excitation. The top TiO_2 layer was also set to 30nm, creating a truncated layer in the periodic structure. The thickness of this layer was chosen due to the limitations in the wavelength range of the experimental setup (≈ 350 to 1700nm). In order to allow the simultaneous excitation of both BSW's in the s polarization near 400nm and plasmonic modes in the infrared range (which would suffer redshift with an increase of external RI), it was verified using transfer matrix simulations that a thickness 30nm would allow an excitation of both surface waves in the wavelength range of the experimental setup (below 20nm no BSW mode exists and above 40nm the SPP appears at wavelengths higher than 1700nm in MDPHC-water interfaces). Figure 4.24 plots the dispersion relation for the structure with $d_1 = 300\text{nm}$ in both polarizations.

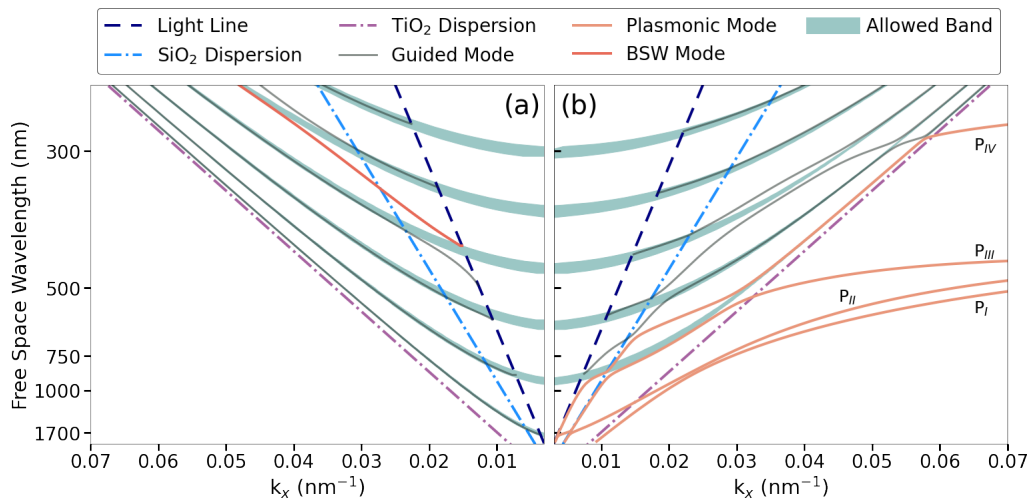


Figure 4.24: Dispersion relation of the proposed structure with $d_1 = 300\text{nm}$. Silver is modelled as a lossless DL metal and $n_{\text{TiO}_2} = 2.7$: (a) s polarization; (b) p polarization.

In Figure 4.24 (a), the analysis of the dispersion diagram is straightforward, and a BSW can be seen propagating in the forbidden band between the third and fourth allowed bands. This dispersion diagram is entirely similar to the dispersion of an all-dielectric PhC due to the absence of plasmonic modes. Nevertheless, in Figure 4.24 (b), the presence of plasmonic modes and the interactions with the guided modes of the structure makes analysis of this polarization significantly harder. A total of four plasmonic modes is seen, of which only two are accessible by excitation with an SiO₂ prism. Due to the high asymmetry of the structure, no mode degeneracy lifting is observed and each dispersion line can be assigned to a specific silver-dielectric interface. The mode with the lowest wavelength (identified as P_I) tends at low wavevectors to the TiO₂ dispersion line and at high wavevectors to $\omega_{TiO_2} = \omega_p / \sqrt{1 + \epsilon_{TiO_2}}$, meaning that it is generated at a TiO₂-Ag interface, and corresponds to a standard SPP formed at the lower interface of the top metal film. On the other hand, the mode identified as P_{II} tends to the SiO₂ dispersion at low k and to ω_{TiO_2} at high k values. This implies that the mode is excited by the SiO₂ prism and is in contact with a TiO₂ layer, thus corresponding to an SPP generated at the top layer of the lower metal film. These modes (P_I and P_{II}) correspond to the bulk modes of the structure and display similar features to the bulk modes analysed in Section 2.4, even though they do not form from a degeneracy lifting process. The mode identified as P_{III} is generated at the light line (vacuum is considered at the last interface of the structure) and tends to ω_{TiO_2} at high k . As such, this mode is excitable using an SiO₂ prism and corresponds to the SPP generated at the top metal interface, which is covered by a small TiO₂ cap layer (even though it has a large penetration in vacuum), justifying why it tends to ω_{TiO_2} .

The last plasmonic mode, identified as P_{IV} is of harder analysis. While it is generated at the light line (thus being accessible) it tends to $\omega_{SiO_2} = \omega_p / \sqrt{1 + \epsilon_{SiO_2}}$ at high k , meaning that the mode penetrates into the prism/substrate. Nevertheless, a strong interaction of this mode with the MDPhC band structure is seen, with it occupying the fundamental band and pushing the fundamental mode¹ (TM₀) to the first band. On the other hand, the TM₀ mode pushes the TM₁ mode to the forbidden band of the PhC. This interaction between different modes corresponds to new phenomenology that hasn't been reported previously (as far as the authors are aware), and requires further study.

The proposed structure was studied for different thicknesses of d_1 . Figure 4.25 presents a similar dispersion diagram but for the case of $d_1 = 100\text{nm}$.

¹Avrustky et al. [100] argue that in metal-dielectric structures the common denomination TM_x does not work in metal dielectric structures due to the fact that the plasmonic modes also have nodes, making classification harder. We decided to keep the traditional nomenclature for the guided modes, even though the TM₀ mode may display nodes due to the presence of the plasmonic modes.

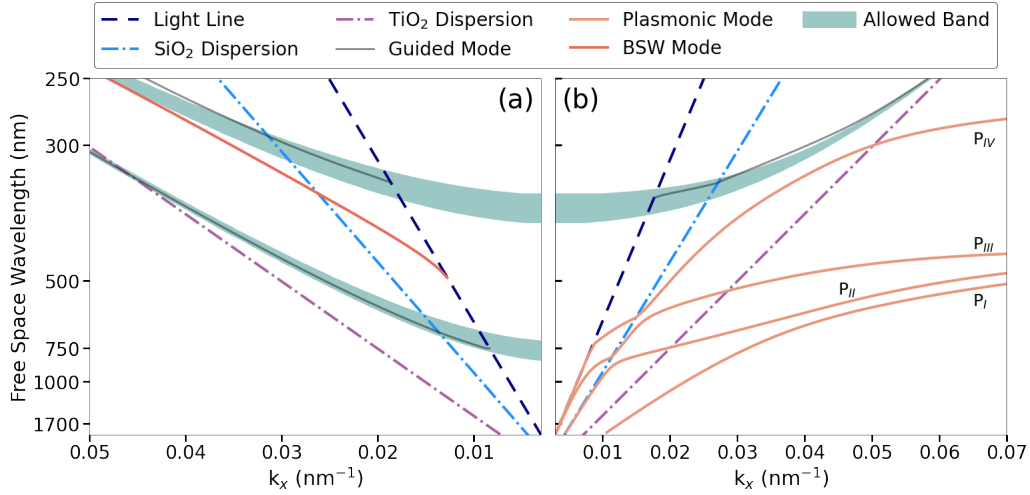


Figure 4.25: Dispersion relation of the proposed structure with $d_1 = 100\text{nm}$. silver is modelled as a lossless DL metal and $n_{\text{TiO}_2} = 2.7$: (a) s polarization; (b) p polarization.

Comparing Figures 4.24 and 4.25 it is possible to observe the effect of the thickness of the first TiO_2 layer. While the plasmonic modes are still present, the number of guided modes is greatly reduced, as expected. Nevertheless, it can be seen that the BSW mode is still supported between the fundamental and first allowed bands. As will be seen, even for thicknesses as low as $d_1 = 50\text{nm}$ the BSW mode is still visible, enabling excitation of this surface wave even in very thin multilayer structures.

Figure 4.26 plots the magnitude of the electric (TE) and magnetic (TM) fields inside the MDPHC structure for the BSW and accessible plasmonic modes. In this case, losses were included in the silver layers, with the optical properties being taken from [190].

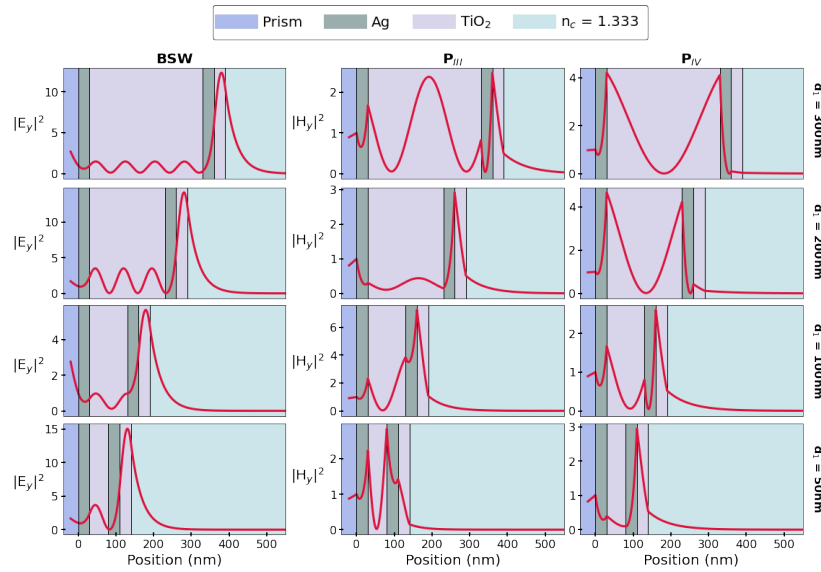


Figure 4.26: Magnitude of the transverse component of the fields inside the MDPHC structure for the different surface modes.

In Figure 4.26, the BSW modes (first column) behave similarly to the case of all-dielectric PhCs, where the field is considerably magnified in the last layer. This implies that excitation of BSW modes in MDPHCs is very similar to that of PhCs, assuming low metal losses. Regarding the plasmonic modes, analysis of the fields is not trivial. For the P_{III} mode, it can be seen that higher thicknesses of the TiO_2 layer have increased magnification of the field, in principle corresponding to higher external RI sensitivities. The opposite effect is seen in the P_{IV} mode, where decreasing d_1 leads to an increase in the field at the MDPHC - dielectric interface. This difference in behavior between the different modes may be of interest for applications in optical sensing.

Analysing the field configuration of the two plasmonic modes leads to the conclusion that while the dispersion relation hints at where the modes are formed (in particular, in which interface) there is a strong interaction with other layers within the MDPHC structure, and assigning a particular interface to the plasmonic mode may be a particularly narrow manner of describing such complex interactions.

4.3.3 Experimental Results

Figure 4.27 shows the experimental results obtained with the MDPHC structure with $d_1 = 300\text{nm}$ in the p polarization.

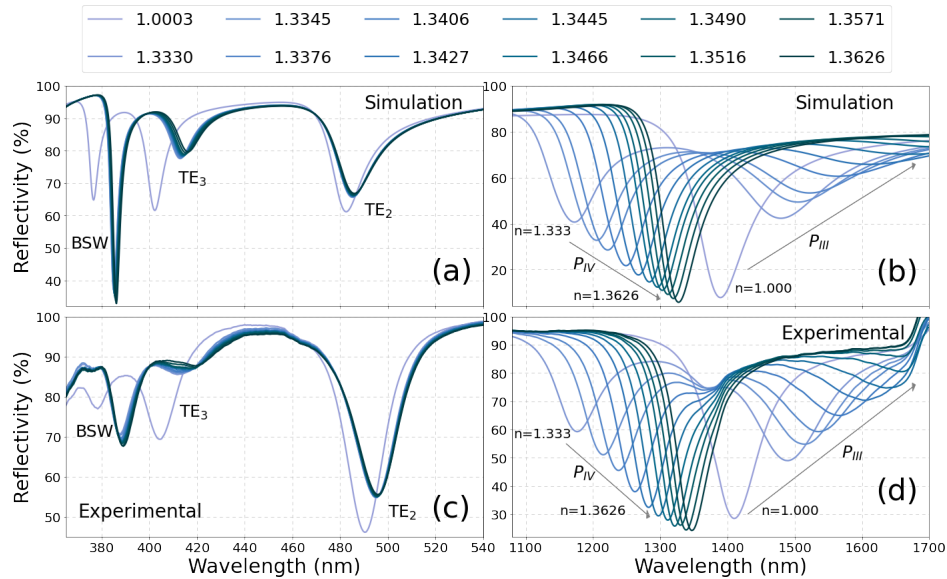


Figure 4.27: Simulated and experimental reflection spectra of the $d_1 = 300\text{nm}$ MDPHC structure: (a) Experimental, TE modes; (b) Experimental, TM modes; (c) Simulation, TE modes; (d) Simulation, TM modes.

Figure 4.27 shows excellent agreement between the experimental and simulation results, especially in the peak wavelength of each band. In the case of the s polarization, the BSW mode is observed near the band edge marked by the TE_3 mode, and shows a peak considerably less

sharp than predicted in the simulations, most likely due to losses associated with the Ag layer. Regarding the p polarization, the two plasmonic modes are clearly visible and display opposite responses to variations of the external RI. Both modes show very high RI sensitivity which is characteristic of SPPs. These results show that simultaneous excitation of two different surface modes (BSW and SPPs) is possible, even though in the chosen configuration these need to lie in opposite regimes of the wavelength range.

Figure 2 plots the experimental results for the case of $d_1 = 50\text{nm}$. The spectra for the cases of $d_1 = 200, 100\text{nm}$ are included in the Appendix.

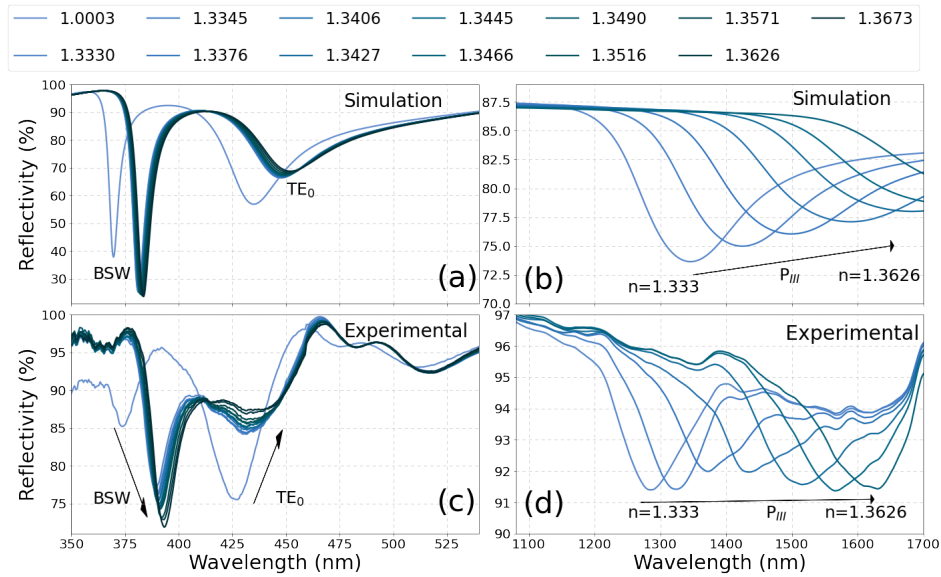


Figure 4.28: Simulated and experimental reflection spectra of the $d_1 = 50\text{nm}$ MDPHC structure: (a) Experimental, TE modes; (b) Experimental, TM modes; (c) Simulation, TE modes; (d) Simulation, TM modes.

Figure 2 also presents two surface modes, one plasmonic and the BSW mode. Again, excellent agreement between experimental and simulation results is seen. In this case, the BSW mode presents an even narrower dip than in Figure 4.27, and also shows a larger intensity response to refractometric variations. In the case of the P_{III} mode, a very high sensitivity is observed, and the mode quickly falls out of the wavelength range allowed by the spectrometer.

Given the experimental results obtained for all the structures, the sensitivity and FoM can be calculated. The results were compared with a structure composed of an Ag layer of 50nm capped by a TiO_2 layer of 30nm deposited on SiO_2 , which corresponds to a conventional Ag plasmon located in the same region of the spectrum as the plasmonic modes of the MDPHC. This mode serves as comparison to the P_{III} mode due to their similar nature (both excited with an SiO_2 prism and tending to ω_{TiO_2}). The reflection spectra obtained for this structure are also presented in Appendix. Figure 4.29 plots the sensitivity of the plasmonic modes.

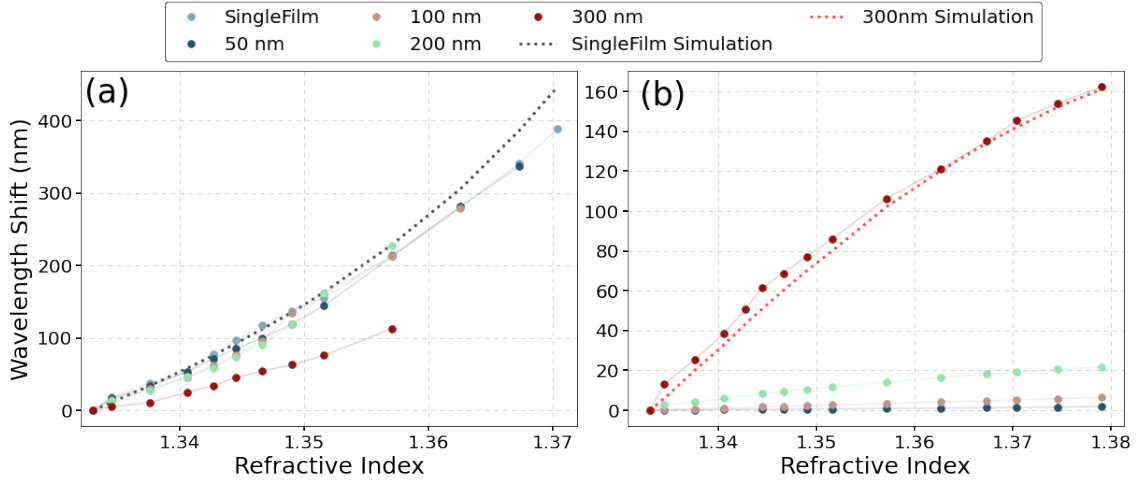


Figure 4.29: Wavelength shift of the plasmonic modes as a function of the external RI. (a) P_{III} mode; (b) P_{IV} mode.

Figure 4.29 (a) presents the comparison of the P_{III} mode for different thicknesses with the SPP mode of the single Ag-TiO₂ structure. It can be seen that the wavelength shift of the structures (except for 300nm) is very similar, which is to be expected given that this mode is generated at the top metal interface of the MDPHC. Nevertheless, a small decrease in wavelength shift (which translates into a decrease in frequency) with the increase of d_1 is also visible, as expected from the analysis of Figure 4.26. As d_1 increases, the field that penetrates the analyte decreases and consequently the mode will be less sensitive. This is particularly noticeable in the $d_1 = 300\text{nm}$ case, where the wavelength shift decreases considerably.

Regarding the P_{IV} mode, represented in Figure 4.29 (b), the opposite process is seen. A large increase in sensitivity is seen for the $d_1 = 300\text{nm}$ structure, and the sensitivity (which is the derivative of the wavelength shift) is higher in water than in higher RI values. This behaviour is in agreement with the simulations (represented in a dashed line) and is very similar to the behaviour of guided modes. In the case of guided modes, an increase in the external RI increases the effective index, leading to a larger confinement. The same is seen here, which could be explained by the fact that the mode is generated at the first metal interface of the MDPHC structure, interacting with the thick TiO₂ layer. Further research is needed into understanding the behaviour of this mode, not just for comprehension of its nature but due to the possibility of applications in gas sensing due to the sensitivity to low RI values. Table 4.6 summarizes the analysis of sensitivity (near the water RI), FWHM and FoM for the P_{III} modes of the different structures.

Table 4.6: Summary of the sensitivity, FWHM and FoM for the P_{III} mode of the metal dielectric structures analysed.

d_1 (nm)	Sensitivity (nm RIU $^{-1}$)	FWHM (nm)	FoM (RIU $^{-1}$)
300	$(4.0 \pm 0.3) \times 10^3$	83.55	47.9
200	$(6.4 \pm 0.3) \times 10^3$	101.21	63.0
100	$(6.6 \pm 0.3) \times 10^3$	129.99	51.0
50	$(7.2 \pm 0.3) \times 10^3$	83.86	85.3
SPP Film	$(8.2 \pm 0.5) \times 10^3$	79.9	103.2

The P_{III} modes seen display very high sensitivity, but always below the conventional metal dielectric implementation. While a clear reduction in the FoM is seen, the proposed structure might display some advantages due to the increased number of modes, which could allow better information extraction from analysing the response of multiple bands [133]. Nevertheless, it is interesting to notice that the lower the thickness of the dielectric, the closer the performance of the P_{III} mode is to the metal dielectric implementation. In particular, the 50nm structure seems promising, due to the presence of a very sensitive P_{III} mode and a well defined BSW, while being of easy fabrication due both to low thickness and reduced number of layers.

The sensitivity of the P_{III} mode of the metal dielectric structures represents an improvement over other metal dielectric structures using a similar configuration. Recently, Gao et al. demonstrated experimentally an HMM sensor (Ag/TiN $_x$ O $_y$ on BK7 substrate) with a sensitivity of 2475.20 nm RIU $^{-1}$ and a FoM of 18.56 [108]. The Ag - TiO $_2$ structures presented in this work display higher sensitivities to RI variations, as indicated in Table 4.6. Further research is needed to develop structures with sensitivities closer to more refined optical structures such as hypergrating and nanopillars implementations [118, 119], which have sensitivities up to one order of magnitude higher. Table 4.7 summarizes the same analysis for the P_{IV} modes of the different structures.

Table 4.7: Summary of the sensitivity, FWHM and FoM for the P_{IV} mode of the metal dielectric structures analysed.

d_1 (nm)	Sensitivity (nm RIU $^{-1}$)	FWHM (nm)	FoM (RIU $^{-1}$)
300	$(5.0 \pm 0.2) \times 10^3$	63.33	78.3
200	$(6.2 \pm 0.4) \times 10^2$	43.48	14.2
100	$(1.4 \pm 0.4) \times 10^2$	41.30	3.5
50	$(3.7 \pm 0.1) \times 10$	36.22	1.0

In Table 4.7, it is clearly seen the large increase in sensitivity in the $d_1 = 300$ nm structure. As mentioned previously, further study is needed to understand the nature of this mode. It is interesting to observe that this mode displays the second highest FoM of all MDPHC structures, further explaining the interest this structure may have in sensing applications. Table 4.8 presents the analysis of the BSW modes for the different MDPHC structures.

Table 4.8: Summary of the sensitivity, FWHM and FoM for the BSW mode of the metal dielectric structures analysed.

d_1 (nm)	Sensitivity (nm RIU ⁻¹)	FWHM (nm)	FoM (RIU ⁻¹)
300	$(5.5 \pm 0.4) \times 10$	10.60	6.2
100	$2.1 \pm 0.4 \times 10^2$	13.83	14.9
50	$1.20 \pm 0.05 \times 10^2$	13.1	

In Table 4.8, the $d_1 = 200\text{nm}$ case is not presented because the BSW mode is very shallow, and quantification of sensitivity and FWHM is very hard. From comparison of Table 4.8 with 4.4, it can be seen that for the modes approximately in the same wavelength range the FoM is very similar, leading to the conclusion that BSWs excited in MDPhCs do not show any disadvantage in comparison with conventional PhCs.

Chapter 5

Conclusions

A theoretical and experimental study of the application of ESWs for optical sensing is reported. Two different ESWs are the subject of study, SPPs (generated at metal dielectric interfaces) and BSWs (generated at PhC dielectric interfaces).

In 1D layered structures, the TMM formalism provides simple tools for characterization of the optical properties of multilayer stacks, in particular by allowing the calculation of reflection and transmission spectra, dispersion relations and field plots of a given structure, which is presented in Chapter 2. The application of SPPs and BSWs in optical sensing is then detailed, firstly by explaining how the properties of the surface wave change in the presence of perturbations and then by calculating the optical response of the ESW bands using perturbation theory. In the case of BSWs, the presented application of perturbation theory in the calculation of the sensitivity response constitutes novel results, contributing for the recent interest and growing knowledge in BSW based sensors. Lastly, the optical properties of MDPHCs are explored using the concepts associated with BSWs and SPPs. The interesting phenomenology observed in MDPHCs is simplified by performing a similar analysis to that made for PhCs. In this case, both guided and plasmonic modes create allowed bands of propagation in the PhC, leading to remarkable properties that find application in many areas of optics and photonics. This band analysis ends with the conclusion that both surface modes can be simultaneously excited in a MDPHC.

The presented work is divided into three main steps: simulation of the optical properties of the structures, device fabrication and characterization, which are detailed in Chapter 3. Fabrication of the devices was made using RF Magnetron Sputtering, and both the deposition technique and the available setup are described. A considerable part of the work performed regarded the improvement of the sputtering setup, and these improvements are reported by demonstrating the increase in film quality using SEM analysis. This process allowed the fabrication of high quality thin films which are of the utmost importance, especially in high loss regimes such as MDPHCs. The experimental setup for ESW excitation is then detailed, which consists of a 3D printed setup using the Kretschmann configuration. This setup incorporates all the needed equipment for ESW excitation in a single 3D printed piece, allowing simple replication and multiplexing

with similar systems. Lastly, the simulations were implemented using home made code based on the TMM formalism, allowing the calculation of the complete optical response of an arbitrary multilayer stack, whether on planar substrate or on a MMF. The TMM simulations were also implemented by taking into consideration the experimental setup, which displays nuances (such as angular broadening) that need to be taken into account for a realistic description of the sensor's behaviour.

The deposition and excitation setups are then validated by testing different plasmonic and BSW configurations and comparing with the TMM simulations. Excitation of SPP modes in four different metals is reported - gold, silver, copper and aluminium, and their performance as refractometric sensors is characterized. While these results serve mainly as setup validation, they already contain relevant results in plasmonic applications, where a large interest of shifting from noble metals such as gold (very expensive) to alternative metals such as aluminium and copper has been verified recently. In particular, the performance of aluminium in the FoM metric (44) was more than double of gold (21), giving excellent perspectives for fabrication of a new generation of inexpensive plasmonic sensors. The combination of a silver SPP covered by a silicon cap layer was also tested, displaying a large improvement in the sensitivity and a FoM of 102, which constitutes an excellent result for application of SPP modes in the NIR. Further research into the combination of plasmonic metals and high RI dielectric or semiconductor materials is needed in order to test how much further the FoM can be increased and the implications in chemical and bio sensing. The sensitivity characterization of plasmonic modes was also tested in MMFs for the gold and silver SPPs, allowing integration with other projects within the research group. In this case, the silver covered MMF achieved a FoM of 83, one of the highest achieved so far for such a simple structure. These results need further study not just to understand the nature of this sensitivity increase but also for relevance in sensor development, due to the fact that the Ag fiber presents an extremely high FoM for an MMF implementation. Comparing with literature values, the best performing MMF implementations consist of D-shaped fiber sections with thin films deposited on top, achieving FoM of 80 for a gold film [193] and 118 for a gold-dielectric-gold implementation [194]. The presented MMF configuration is of easier fabrication and has a similar high performance (FoM of 83), thus justifying the need for further research.

The experimental setup was also used to test the observation of BSWs in planar substrates and optical fibers. These measurements validated the experimental setup for observation of BSWs in both polarizations, where agreement was observed in comparison with the simulations. These preliminary results allowed the design of a study to experimentally test the calculation of BSW refractometric sensitivity using perturbation theory. Good agreement was shown between the TMM simulations, the PT approach and the experimental results for both polarizations, thus responding to a recent interest in the literature of reducing the sensitivity of BSW sensors to a function of physical parameters. These results may find application in the optimization of PhC design for optical sensors, where so far only numerical or semi-numerical optimizations have been reported [186, 79, 78].

Lastly, the simultaneous excitation of BSWs and SPPs is reported in a MDPHC. Given the previous study of metal dielectric periodic structures, the similarities between PhCs and MDPHCs are demonstrated by the observation of both BSW and guided mode resonances in the s polarization. At the same time, the behaviour of the fabricated MDPHCs in the p polarization displays four different plasmonic modes (of which only two are accessible in the current experimental setup), confirming the simultaneous observation of BSWs and SPPs. The interaction between plasmonic and guided modes of the MDPHC demonstrates new phenomenology, in particular with the guided modes being pushed off the allowed bands by the plasmonic modes. Further research into these interactions is needed in order to understand them and analyse their potential application in optical devices. The performance of the plasmonic and BSW modes is then experimentally tested for RI variations. While a slight decrease of FoM is seen between a conventional silver metal film and the MDPHC plasmonic modes is seen, the proposed structure may display considerable advantages. In particular, the simultaneous analysis of an SPP and a BSW mode may be of interest in biosensing, where both modes will respond differently, allowing for better referencing and extraction of more information.

While the presented studies establish a foundation which may allow for future research into ESWs, much work is still needed. The development of an experimental setup with variable angle and microfluidic integration, which was not possible to implement due to component delays, is of great importance for achieving truly high performance optical sensors. The usage of BSWs for detection of biological targets, which constitutes one of the main objectives associated with the research project, is also a future goal which will be achieved by building upon the knowledge developed for BSW excitation. At the same time, further study is needed into understanding how the properties of MDPHCs can be used to improve optical sensors. The characterization of the optical response of these structures under refractometric, adsorption and thermal variations is of great importance for the development of independent, self-referenced high performance biosensors, which may find application in both technological and scientific contexts.

Appendix

Sensitivity of Bloch Surface Waves

In this appendix, the calculation of the refractometric and adsorption sensitivity are detailed using a first order perturbation theory approach. The tangential fields of a BSW are given by:

$$\Psi(z) = \begin{cases} \Psi_K(z)e^{iKz}, & z > 0 \\ \alpha e^{q_0 z}, & z < 0 \end{cases} \quad (1)$$

Calculation of the perturbation to the effective index Δn_{ef} is given by

$$\Delta(n_{ef}^2) = \begin{cases} \frac{\frac{\lambda^2}{4\pi^2} \int_{-\infty}^{+\infty} \Delta\varepsilon(z) \left(\frac{1}{\varepsilon(z)} \frac{dH_y(z)}{dz} \right)^2 dz - n_{ef}^2 \int_{-\infty}^{+\infty} \Delta\left(\frac{1}{\varepsilon(z)}\right) H_y^2(z)}{\int_{-\infty}^{+\infty} \frac{1}{\varepsilon(z)} H_y^2(z) dz}, & \text{for TM Modes} \\ \frac{\int_{-\infty}^{+\infty} \Delta\varepsilon(z) E_y^2(z) dz}{\int_{-\infty}^{+\infty} E_y^2(z) dz}, & \text{for TE Modes} \end{cases} \quad (2)$$

with $\Delta(n_{ef}^2) = 2n_{ef}\Delta n_{ef}$.

Refractometric Sensitivity

In this case, $\Delta\varepsilon(z) = 2n\Delta n$, where n is the external RI; and $\Delta(\varepsilon(z)^{-1}) = -\Delta\varepsilon/\varepsilon^2 = -2\Delta n/n^3$.

TE Modes

The calculations are divided in the denominator and numerator. The numerator is given by:

$$\int_{-\infty}^0 2n\Delta n\alpha^2 e^{2q_0 z} dz = \frac{n\alpha^2}{q_0} \Delta n \quad (3)$$

On the other hand, the denominator is:

$$\int_{-\infty}^0 \alpha^2 e^{2q_0 z} dz + \int_0^{+\infty} |\Psi_K(z) e^{iKz}|^2 dz = \frac{\alpha^2}{2q_0} + P^{TE} \quad (4)$$

Using these two calculations, the effective index sensitivity is calculated by:

$$\frac{\partial n_{ef}}{\partial n} = \frac{1}{n_{ef}} \frac{n}{1 + 2q_0 \frac{P^{TE}}{|\alpha^2|}} \quad (5)$$

TM Modes

The calculations are divided in the three integrals, one in the denominator and two in the numerator. The first integral of the numerator is given by:

$$\frac{\lambda^2}{4\pi^2} \int_{-\infty}^0 2n \Delta n \left(\frac{\alpha q_0 e^{q_0 z}}{n^2} \right)^2 dz = \frac{\lambda^2}{4\pi^2} \left(\frac{\alpha^2 q_0}{n^3} \right) \Delta n \quad (6)$$

The second term in the numerator is:

$$n_{ef}^2 \int_{-\infty}^0 \frac{-2\Delta n}{n^3} \alpha^2 e^{2q_0 z} dz = -\frac{n_{ef}^2 \alpha^2}{n^3 q_0} \Delta n \quad (7)$$

The term in the denominator is:

$$\int_0^{+\infty} \frac{|\Psi_K(z) e^{iKz}|^2}{n_i} dz + \int_0^{+\infty} \frac{\alpha^2 e^{2q_0 z}}{n^2} dz = P^{TM} + \frac{\alpha^2}{2n^2 q_0} \quad (8)$$

Equating all terms, the effective index perturbation is obtained:

$$\frac{\partial n_{ef}}{\partial n} = \frac{2n_{ef}^2 - n^2}{n_{ef}} \frac{1}{n + 2n^3 q_0 \frac{P^{TM}}{|\alpha^2|}} \quad (9)$$

Adsorption Sensitivity

In this case, $\Delta \varepsilon(z) = (n_F^2 - n^2)$, where n is the external RI; and $\Delta(\varepsilon(z)^{-1}) = (n_F^{-2} - n^{-2})$. Notice that this value of $\Delta(\varepsilon(z)^{-1})$ because the RI of the adlayer is generally high, meaning the differential cannot be calculated normally [133].

In the calculations, the following integral is used

$$\int_{-d_F}^0 e^{2q_0 z} dz = \frac{1 - e^{2q_0 d_F}}{2q_0} \approx \frac{2q_0 d_F}{2q_0} = d_F \quad (10)$$

where in the approximation the term $1 - e^{2q_0 d_F}$ is Taylor expanded because $q_0 d_F \approx 0$ (the penetration depth is much larger than the adlayer thickness).

TE Modes

The calculations are divided in the denominator and numerator. The numerator is given by:

$$\int_{-d_F}^0 (n_F^2 - n^2) \alpha^2 e^{2q_0 z} dz = (n_F^2 - n^2) \alpha^2 d_F \quad (11)$$

On the other hand, the denominator is:

$$\int_0^{+\infty} \frac{|\Psi_K(z) e^{iKz}|^2}{n_i} dz + \int_0^{+\infty} \frac{\alpha^2 e^{2q_0 z}}{n^2} = P^{TM} + \frac{\alpha^2}{2n^2 q_0} \quad (12)$$

By equating all the terms and performing some algebra, the final result is obtained:

$$\frac{n_F^2 - n_0^2}{n_{ef}} \frac{1}{\frac{1}{q_0} + 2 \frac{P^{TE}}{\alpha^2}} \quad (13)$$

TM Modes

The calculations are divided in the three integrals, one in the denominator and two in the numerator. The first integral of the numerator is given by:

$$\frac{\lambda^2}{4\pi^2} \int_{-d_F}^0 (n_F^2 - n^2) \left(\frac{\alpha q_0 e^{q_0 z}}{n^2} \right)^2 dz = \frac{4\pi^2}{\lambda^2} \frac{(n_F^2 - n^2) \alpha^2 q_0^2}{n^4} d_F \quad (14)$$

The second integral in the numerator is:

$$n_{ef}^2 \int_{-d_F}^0 (n_F^{-2} - n^{-2}) \alpha^2 e^{2q_0 z} = n_{ef}^2 \alpha^2 (n_F^{-2} - n^{-2}) d_F \quad (15)$$

The integral in the denominator is

$$\int_0^{+\infty} \frac{|\Psi_K(z) e^{iKz}|^2}{n_i} dz + \int_0^{+\infty} \frac{\alpha^2 e^{2q_0 z}}{n^2} = P^{TM} + \frac{\alpha^2}{2n^2 q_0} \quad (16)$$

By equating all the terms and performing some algebra, the final result is obtained:

$$\frac{\partial n_{ef}}{\partial d_F} = \frac{n_{ef}^2 (n_0^{-2} + n_F^{-2}) - 1}{n_{ef}} \frac{(n_F^2 - n_0^2)}{\frac{1}{q_0} + 2n_0^2 \frac{P^{TM}}{\alpha^2}} \quad (17)$$

Metal-Dielectric Photonic Crystals

The plots of the MDPHCs with $d_1 = 200$ and 100nm are here presented.

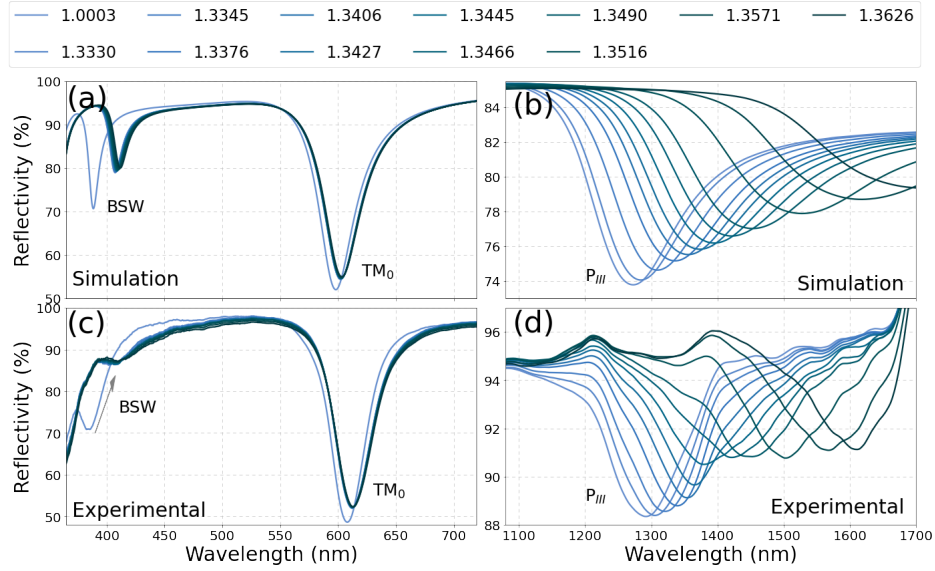


Figure 1: Simulated and experimental reflection spectra of the $d_1 = 100\text{nm}$ MDPHC structure: (a) Experimental, TE modes; (b) Experimental, TM modes; (c) Simulation, TE modes; (d) Simulation, TM modes.

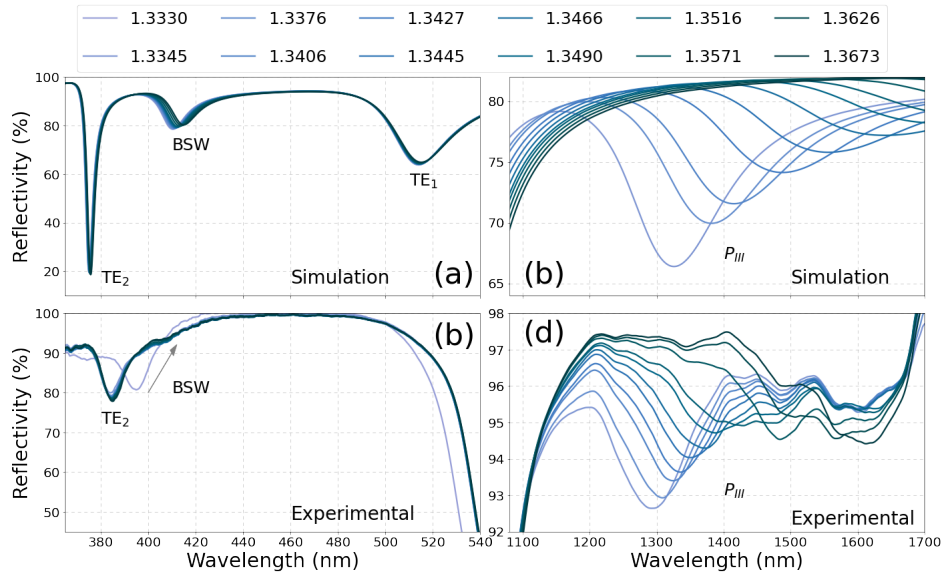


Figure 2: Simulated and experimental reflection spectra of the $d_1 = 200\text{nm}$ MDPHC structure: (a) Experimental, TE modes; (b) Experimental, TM modes; (c) Simulation, TE modes; (d) Simulation, TM modes.

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