Structured Metallic Films for Enhanced Light Transmission and Absorption

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Abstract

Photonic devices such as light emitters, detectors, solar cells etc. are playing increasingly important roles in modern society. Yet their structures and designs are still under constant improvement, driven mostly by advances in material science and progress in integration techniques. A common challenge in these devices is to precisely manage transmission and absorption of light when it enters or escapes active regions. In certain devices it is even required to have both high optical transmission as well as high electrical conductivity. The current thesis investigates how structured metallic films can be devised to meet these challenges. Our work demonstrates that nanostructured noble metals can be tailored as either transparent or highly absorptive at wavelengths of interest, with or without electrical conductivity.

In the first part of this work, metallic photonic crystals in the form of a thin gold film with an array of holes were fabricated with various geometrical parameters (hole size, pitch and metal thickness) on different substrate materials to investigate the impact of each parameter on the transmittance spectra at mid- to long-wave infrared wavelengths. Pitch size is shown to be the dominating factor for the high-transmittance band positions. Fill factor and metal thickness collectively define the selectivity of the pass bands. The selective transmission of infrared light can be used to improve the performance of infrared detectors. In the second part of this work, a thin-film multilayer structure based on two coupled metal-insulator-metal optical resonators was investigated for achieving a transparent conductor at visible wavelength range. The fabricated silver-based sample has a figure of merit (transmissivity-over-resistance) comparable to that of the traditionally used indium tin oxide. Such structures can potentially be used in light-emitting diodes and displays. In the third part of this work, a thin gold nanoparticle layer is obtained from a thermal annealing process. The interplay between this nanoparticle layer and a substrate metal reflector gives rise to broadband extinction of light at the near-infrared wavelength range. Specular and diffuse reflectances were singled out. Samples with high absorption or high diffuse reflection are identified. The structures can potentially be incorporated in solar cells as diffuse back reflectors or as spectrally selective absorbers for solar thermal collectors. In the fourth part of this work, the possibility of using a metal-insulator-metal structure (based on titanium, alumina, and aluminum) for achieving artificial coloration is explored. Through a diffusion-assisted deposition procedure, the dielectric spacer has a laterally varying thickness. Thereby the sample exhibits a continuum of visible colors. The reflectance spectra of the fabricated sample in the visible range were measured, and agreement to theoretical calculation is found to be very good. The artificial colors can be patterned at various geometries. Their potential application, besides functioning as spectrally selective absorbers in optoelectronic devices, can be used for security applications of consumer and artistic products.
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List of papers included in this thesis

Paper I

Author’s contribution: All fabrication and characterization, part of design, major part of writing.

Paper II

Author’s contribution: All fabrication and characterization, part of design, major part of writing.

Paper III

Author’s contribution: All fabrication and characterization, major part of writing.

Paper IV

Author’s contribution: Involved in fabrication and manuscript writing.
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Chapter 1

Introduction

Photonic or light-related technologies are responsible for high-speed transmission of information, energy harvesting, illumination, displays, information capturing, material processing, sensing etc [1-3]. Photonics is becoming a more and more important element that is deeply integrated in our modern society. Modern photonic devices such as light-emitting diodes, displays, solar cells, are still under constant improvement mainly owing to advances in either material processing or integration techniques. The advent of nanotechnology in recent years has accelerated the pace of the advancement. Nanotechnology not only miniaturizes device sizes, which most often reduces power consumption, but also introduces new physical properties. On one hand, the newly emerged material properties can help to improve device performance; on the other hand, they can facilitate use of cheaper materials in place of expensive ones for the same or compromised performances. Indeed, increased efficiency and/or reduced fabrication cost are two general driving forces behind the perpetual effort of device improvements. A general challenge in almost all photonic devices is to precisely control light transmission and/or absorption when it propagates into or out of the devices’ active region. For example, high light transmission is desired for light-emitting diodes; whereas high absorption of infrared light is required for effective detection of heat sources in bolometers. In displays and solar cells, it is even required for a material to have simultaneously high transparency and high electrical conductivity. In recent years, it is seen that more and more work rely on nanostructured materials to manage such requirements of light-matter interaction.

In this thesis, structured metallic thin films are investigated for enhanced transmission, absorption, and even scattering of light. Metals in bulk are usually not transparent from visible up to infrared light. However when they are nanostructured, especially if thicknesses of metal films are comparable to the skin depth at the relevant light frequency, the overall structured metal film can be made transparent. Nanostructured metals also exhibit localized or extended plasmon resonances; they can be exploited for achieving near 100%
light absorption at optical wavelengths that are dependent on structural parameters. Metals are natural electrical conductors. Therefore, through proper design, the resultant composite film can be both optically transparent and electrically conducting. The efforts made in this thesis were divided into two major parts concerning light transmission and light absorption. Enhanced light transmission is discussed in Chapters 2 and 3 and the efforts targeting customized light absorption in Chapters 4 and 5. In each chapter a certain type of metallic nanostructure is proposed as an alternative to currently available options; structural design, fabrication, and characterization are presented; results are discussed, and if applicable, compared to existing options for certain intended applications. An overview of the whole work will be given below.

The performance of infrared detectors depends heavily on infrared light absorption and spectral selectivity. The wide range (from near-infrared up to long-wave infrared) Mercury-Cadmium-Telluride (MCT) detector has fast response and excellent efficiency when coupled with a stable cooling system. The need for a cooling system restricts the application potentials and therefore much research is currently being done on room temperature detectors. The micro-bolometer on the other hand is a relatively low cost, low power and stable thermal detector. However being a thermal detector, it is inherently slow, because of being constrained by thermal dissipation. It also has its own disadvantages of challenging manufacturing process and integration techniques. It also does not meet the high sensitivity and low noise level of cooled detectors. The downsides of using the two most commonly operated infrared detectors have led to advances in quantum-confined detectors. This new generation of detectors also has further enhancements needed regarding their noise sensitivity and cooling accessories [3,4]. Integrating a well-designed metallic photonic crystal structure on top of a quantum-confined detector can potentially decrease noise level and enhance detection efficiency by working as a band-pass filter.

Another field relevant to this thesis is transparent conductors. Transparent conductors are extensively used as the passive top layer integrated to active devices composed of photodetectors such as solar cells, windscreen heaters and displays. Indium tin oxide (ITO) currently dominates the wide application variety of transparent conductors in visible wavelength range. From a
manufacturing perspective, like the other similar oxides, ITO films are sensitive to deposition process techniques when it comes to film quality and characteristics [5]. Scarcity of Indium has inherently increased the cost of using ITO in different applications. Restricted by ITO price and film conductance, efforts have been made to either enhance its characteristics as a transparent conductor or to replace it with a cheaper yet relatively effective alternative with desired optical and electrical characteristics. In order to improve the conductivity of ITO without rigorously deteriorating its transparency, one successful technique has been introducing very thin metal films like silver and gold into its structure [5,6]. Engineered materials present many possible alternatives for replacing ITO. One option is graphene-based films. In spite of graphene’s conducting characteristics being worse than that of ITO, research was performed on this alternative based on its potential in innovative printed electronics [7]. In this thesis a multilayered structure based on two coupled metal-insulator-metal resonators is investigated for achieving wide transmittance band in the visible wavelength range. The figure of merit defined as the ration between transparency and resistance has been proven to be comparable to that of ITO. It is possible to use the proposed structure in various large-area and cost-efficient applications as a transparent conductor.

Energy harvesting with an emphasis on sustainability brings us to yet another popular research field where scientists are struggling with efficiency. Although solar cells are a relatively established method of energy harvesting, its structure and material content are still under rapid development. In spite of their sustainability advantage, they need to be improved in terms of cost-effectiveness in order to compete with the high availability of conventional energy resources [1]. Focusing on the top-down approach, one way of enhancing the performance of solar cells is to integrate a light-scattering layer into them. In solar thermal collectors, one would like to directly convert light into heat through a broadband light absorber; we proposed in this thesis a three-layer structure, which has a top single layer of sub-wavelength gold nanoparticles, in the middle a dielectric spacer, and in the bottom an aluminum reflector. The overall metallic nanostructure behaves as a strong light absorber or scatterer that can be used in many applications like solar cells or solar thermal collectors. The absorption profile of the composite film is tailored by different geometrical parameters and material properties. The top-layer gold nanoparticles are made through a thermal annealing process. This
makes the fabrication process less complex and less time consuming and therefore more cost effective than other complex nanofabrication alternatives such as optical lithography, electron-beam lithography, nanoimprinting [8,9].

The last area investigated in this thesis is artificially fabricated colors. The motivation for pursuing this study was to verify if structural colors could be made with a very simple material deposition process without any lateral structural patterning. Traditional sources of producing colors are through the use of pigments and dyes. Metal-dielectric material composites possessing optical resonances show high potential for producing artificial colors. Their exact visual appearance can be tailored through their geometrical parameters and material properties. Traditionally relatively complex metamaterial structures are used for achieving structural coloring owing to strong absorption in the visible range [10,11]. In this thesis a simple metal-insulator-metal (MIM) resonator structure is proposed for producing colors. Due to its simple fabrication technique with commonly found metals, this provides a way to effectively produce structural colors over large areas.

This thesis opened with the introduction in Chapter 1. As for the remainder of the thesis, 4 chapters follow, presented in chronological order, each discussing the nanophotonic component proposed to introduce enhancement to a targeted branch of applications. Chapters 2 and 3 are allocated to components with tailored transmittance characteristics whereas Chapters 4 and 5 are about components with specified reflectance profile.

Chapter 2 focuses on the study of photonic crystals integratable to infrared detector. The target range of high transmittance for these metallic structures is the mid-wave infrared and long-wave infrared. The goal in this study has been exploring the compatibility of this photonic crystal fabrication process with the quantum confined photodetector technology; also predicting the effects of this integration on the efficiency and noise level of the photodetectors based on the achieved optical characterization of the proposed structure.
Chapter 3 starts by giving an overview of transparent conductors and continues by introducing the metallic nanostructures made up of double metal-insulator-metal resonators with characteristics of a transparent conductor. In order to fulfill the objective, the structure is designed to have a high transmittance band mainly covering the visible range. Once fabricated and characterized the proposed structure should demonstrate simultaneously high conductance and transparency in comparison with ITO. In this case the proposed structure proves to be a promising potential replacement for the expensive indium-based alternatives taking into account its cost-efficient fabrication process and relatively simple structure.

Chapter 4 is based on metal-insulator-metal resonator structures fabricated with the purpose of gaining high absorption within the near infrared wavelength range. To transform the originally fully reflective resonator to an absorber, the top metal layer needs to be patterned to sub-wavelength structures. With the concept of mass production and cost efficient fabrication process, thermal annealing was chosen as the patterning method. In this chapter the fabrication of the structure is explained in details. The optical characterization results are then presented as a proof of concept that this structure has a very high absorption within the infrared range. This makes the proposed component a potential candidate for integration into solar cells for energy harvesting purposes.

Chapter 5 introduces artificial color fabrication through tailoring the metal-insulator-metal resonator specifications and hence the reflectance profile of the metallic nanostructure. The shield used in the fabrication procedure gives a twist to the outcome of this experiment by producing a continuous range of colors.

The thesis closes with Chapter 6 where the discussions are wrapped up into a brief conclusion and a future work is proposed as the continuation of the works presented in this thesis.
Chapter 2

Infrared radiation transmission through metallic photonic crystals

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In this chapter the study of metal-based photonic crystals is presented starting with an overview on photodetectors and photonic crystals in 2.1 and 2.2 respectively. In 2.3 the fabrication methodology is discussed. This sub-section is followed by the results and discussion of this study in 2.4. The chapter continues by explaining the future work in 2.5. Section 2.6 rounds up the chapter by a brief conclusion.

2.1 Overview of infrared photodetectors

The increasing need of detecting signals in the infrared spectrum stems from as wide a range of applications such as fiber optical communication, short ranged wireless communication, spectroscopic imaging, night vision imaging, metrology, astronomy and industrial analysis using thermography [3,13]. This wide range of applications demands special characteristics from the detectors such as data bandwidth (e.g. fiber optical communication), durability (e.g. military night vision or tracking systems), sensitivity (e.g. chemical spectroscopy), device size, cost and spectral range. As applications of IR-detectors within civilian and commercial fields become more and more relevant, such as safety systems in the automotive industry, the importance of lowering complexity and cost of the finished devices are critical. Cooled devices using brittle and expensive materials need alternatives.

The development of infrared detection began in the year of 1800 through the work of Herschel as he discovered the thermal energy of light in a spectrum below visible red. During the next century specific thermal infrared detectors were developed, particularly through the work on the thermocouple and bolometer. In 1821 Seebeck discovered the thermoelectric effect that led to the development of the Thermocouple. Eight years later Nobili created the
thermopile by coupling several thermocouples in series. Four years after this Melloni improved the efficiency of the device by using bismuth and antimony as the electrodes. Towards the end of the 19th century Samuel Langley invented the bolometer, a device where the active layers’ resistance is temperature dependent. Langley improved his design based on thin platinum foils to such an impressive degree that it is said he could detect the heat signature of a cow at a distance of over quarter of a mile. After the turn of the century, the photoconductor was invented by Case, but it was not until the Second World War that research on infrared detectors became a priority for many nations. The large amounts of resources used in the research during the cold war led to the use of expensive and scarce materials and finally Honeywell invented a semiconductor IR detector based on Mercury-Cadmium-Telluride that showed excellent results but only when cooled down to very low temperatures [3,14-16]. It has met competition from other technologies such as thermal detectors (such as the micro-bolometer), Schottky barriers and quantum defined structures such as quantum wells and quantum dots [17-19]. While easier to manufacture and showing promise for higher temperature operation, neither of these competitors meet up to the level of performance when it comes to detectivity and responsivity when compared to the MCT and other photoconductors derived from it [16]. This work has focused on the improvement of quantum dot infrared detectors by integration of photonic crystals directly onto the detector. First we will briefly mention the MCT photodetector as well as quantum well infrared detectors to understand the need of a new alternative and what it must address.

2.1.1 Mercury cadmium telluride detector

Mercury Cadmium Telluride (MCT) is a direct bandgap compound semiconductor alloy that has the possibility to be used within a wide wavelength spectrum (up to 25µm). This makes it very important as a photodiode in applications such as astronomy spectroscopy and metrology spectroscopy where both mid-wave infrared wavelength (3-5µm, MWIR) and long-wave infrared wavelength (8-12µm, LWIR) are important [3,4,13]. It’s most important use is for military applications, where it is used within a wide range of critical detection, range-finding and steering applications. One of its most detrimental faults is that optimal operation is at very low temperatures, all the way down to 77K for the LWIR range [3]. Because the cooling
solutions needed to operate these photodetectors are cumbersome and expensive, numerous alternative solutions are being sought to replace it [3,4,20,21].

2.1.2 Quantum well infrared photodetector

Quantum well infrared photodetector (QWIP) is a semiconductor photodetector where the active energy band is restrained by quantum confinement in one dimension. Because the device is based on a quantum mechanical intraband processes in materials with wide bandgaps, simple semiconductor materials such as GaAs/AlGaAs and SiGe/Si can be used to construct the devices. While progress have been made, especially in forming large detector arrays that actually rival MCT systems, signal-to-noise ratio becomes an issue even above 40K [3].

2.1.3 Quantum dot infrared photodetector

Quantum dot infrared photodetector (QDIP) is a structure where all three dimensions are small enough so that its energy bandgap are defined by quantum confinement. Processing the very small structures in a controlled way have proven difficult, especially the need to avoid inducing local defects that affects the bandgap of the structure [14,22-24]. Advancement in epitaxial deposition has made it easier through the formation of coherent islands during deposition. One of the largest advantages of QDIPs over previously discussed devices such as the QWIP or the MCT detectors is that the dark current of the device is expected to be lower than both. QDIPs can be manufactured in dense horizontal and vertical stacks. By small changes in the process between these superstructures, the detector can efficiently become sensitive in multiple wavelength ranges, which increase temperature sensitivity [25-27].

Integrating PhC structures to the QDIPs has shown great enhancement in the light coupled into the active layer hence increasing the detectivity [28-38]. These sub-wavelength structures are introduced in the following section.

2.2 Overview of photonic crystals

The term photonic crystals (PhC) refer to a periodic repetition of two media
with different refractive indices. This study focuses on metallic PhC (mPhC) where one of the two materials involved is a metal. Using metals such as gold (Au), silver (Ag), titanium (Ti), platinum (Pt), chromium (Cr) or copper (Cu) can bring interesting characteristics to the PhC structure. This is due to the interaction between photons and the metal free electrons [39]. When two materials forming the PhC structure have dielectric constants with opposite signs, the incident wave can excite an oscillating wave called the surface plasmon wave (SPW) at the surface, which propagates along the metal surface. When this happens in a patterned metal film, it will give rise to a resonance phenomenon called the surface plasmon resonance (SPR). The SPR can occur at different wavelengths depending on the structure and the materials involved. This can be identified by a dip in the reflectance spectra of the mPhC surface. The wavelength with the highest dip represents the highest intensity of localized wave called the fundamental mode (first harmonic). The wavelength with the second highest intensity dip in the reflection spectra is the higher order mode (second harmonic).

In spite of advances made in IR detectors throughout the past years, the possibility of higher performance and lower cost has focused an increasing amount of research to be done in the field. MCT, QWIP and QDIP detectors are a few of the many detectors investigated. The main approach in order to improve the responsivity and efficiency is the bottom up approach where the detector itself is studied for further developments. However based on the top-down approach the SPR concept integration into the optoelectronic structure could provide enhancement for the responsivity of the detectors (infrared photodetectors in this study). The many applications of infrared (IR) radiation sensing and imaging have made the study of detectors working in this wavelength range and how to make them more efficient into hot research topics. The enhancement is achieved by a increase in the wave interaction with the detector active material due to the localized confinement of the incident wave. Studies performed on SPR integrations into photodetectors have shown significant improvement in the device performance and efficiency based on plasmonic resonance, such as improved optical coupling [28-38]. An advantage of this approach is the possibility of wafer-scale fabrication which makes the process directly usable with current device processes at a reasonable cost.
2.2.1 Motivation

Efforts have been done to make novel and more efficient quantum dot IR detectors [21,28] with higher operation temperature and lower cost. This improvement is made at the cost of the detectors responsivity. It is believed that this can be significantly improved through the integration of the mPhC structures offered in this work, directly onto the devices. It is then believed that the coupling of the mPhC with the quantum dots will improve the IR absorption by directing and keeping the light in the active area of the detector for a longer period. This can be achieved by keeping the surface-plasmon damping coefficient $\alpha$ as given by Equation 2.1 [41].

$$\alpha \approx \frac{4\pi n_d^3}{\lambda k_m^3}$$  \hspace{1cm} (2.1)

$k_m$ is the imaginary part of the metal’s refractive index, while $n$ is the real part of the dielectric film’s refractive index. $\lambda$ is the wavelength that is being observed. An example of this can be shown for a gold mPhC structure on a GaAs substrate in Figure 2.1.

![Figure 2.1: The Surface-plasmon damping coefficient for a gold mPhC on GaAs substrate versus the wavelength.](image)

The principle structure of the integrated IR detector and its operation can be seen in Figure 2.2. The mPhC should be designed and optimized in a way so that its transmission spectrum has good coherence with the absorption spectrum of the quantum dot IR detector.
Figure 2.2: (a) A principle structure of the quantum dot IR detector with integrated mPhC and its operation. In this example ten layers of QDIPs are manufactured on top of each other so that they will have maximum efficiency for when the IR signal is transferred through the device via the mPhC structure [29]. The sizes sketched in this schematic are not proportional to the designed and fabricated structure sizes.

A significant advantage of the mPhC structure is its metallic material which makes it excellent for also being used as the contact interface between the read-out circuit and the detector itself.

2.2.2 Design

The design of this project was based on simulations of transmission spectra done previously [28] in which metallic photonic crystal structure with pitch sizes between 3-4µm and hole diameter of 1 µm were investigated. The chosen substrate was GaAs in the simulated case and the metal (gold) layer 100nm thick. The wavelengths of interest were 2-12 µm which matches the photodetectors suitable for the future work of the fabrication project. Taking this as the basis several samples with variations in pitch sizes, hole diameters, metal thickness and substrate material were fabricated.

2.3 Fabrication methodology

A mass production approach is taken up for fabrication of the samples in this project in order to facilitate the compatibility and the ease of integration into state of the art photodetectors. Two dimensional photonic crystals have been etched into gold thin film layers deposited on double-side polished 4 inch
substrates. Silicon and GaAs were used as the two choices of substrate in this research project. The fabrication process is schematically outlined in Figure 2.3.

![Figure 2.3: The fabrication process schematic [29].](image)

The fabrication process starts with mounting the substrate wafers into the metal deposition chamber. The wafers are first covered with 5nm of Titanium as an adhesive layer and then with gold thin film. The metal deposition is done in electron-beam evaporation chamber (Provac PAK600) at a pressure of $5 \times 10^{-7} \text{ mbar}$ and with deposition rates of $1 \text{ Å/s}$. Once out of the chamber, the wafers are coated by a 1 µm thick positive resist layer (SPR700_1.2) followed by a soft bake. The 1 µm thickness is achieved by two spinning steps of 500rpm for 5seconds followed by 300rpm spin for 30seconds. The resist layer is then patterned through photolithography by exposure to UV light in a XLS 7500/2145 i-line stepper with the magnification of 5:1. The UV exposure dose is 170mJ/cm² (applied at two set of 85mJ/ cm² to increase the structures precision) at the wavelength of 365nm. To complete the patterning the wafers are developed with Shipley Microposit 351 developer. Once developed, the wafers are placed in an oven for post development hard baked in order to form the hard mask needed for etching the pattern into the gold film. A mix of I₂:KI:H₂O with the ratio of 1:4:40 is used for isotropic wet etch process where the pattern on the resist layer is copied to the gold film. The hole diameter is strictly controlled by the etching time. Then the resist layer hard mask is removed using organic contaminate clean namely Acetone and Isopropanol alcohol (IPA). The fabrication process is summarized in Table 2.1.
Table 2.1: The 2-D photonic crystal fabrication process [29].

<table>
<thead>
<tr>
<th>No.</th>
<th>Process step</th>
<th>Recipe</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Metal evaporation</td>
<td>Provac PAK 600 Coating System</td>
<td>5nm Titanium, 50/100/200nm Gold</td>
</tr>
<tr>
<td>3</td>
<td>Resist coating</td>
<td>Positive Resist (SPR700)</td>
<td>1µm resist film thickness</td>
</tr>
<tr>
<td>4</td>
<td>Exposure</td>
<td>XLS stepper</td>
<td>170 mJ/cm²</td>
</tr>
<tr>
<td>5</td>
<td>Developement</td>
<td>Optidev</td>
<td>RFLO20sNoB</td>
</tr>
<tr>
<td>6</td>
<td>PostHardbake</td>
<td>110° C oven, approximately 30min</td>
<td>For achieving higher thermal stability and etch resistance</td>
</tr>
<tr>
<td>8</td>
<td>Etching Gold</td>
<td>(I2 : KI : H2O) Mix(1 : 4 : 40)</td>
<td>Etch time dictates pattern size</td>
</tr>
<tr>
<td>9</td>
<td>Resist Removal</td>
<td>organic contamination removal</td>
<td>Acetone, IsoPropanol</td>
</tr>
</tbody>
</table>

The top view of the fabricated photonic crystal samples is shown in Figure 2.4. The 3-D view made by Atomic Force Microscopy (AFM) is shown in Figure 2.5.

![Figure 2.4: The 2-D top view of the samples demonstrating changes of the diameter size of the holes with respect to etching time [29].](image-url)
Figure 2.5: The top view and the 3-D view of one of the fabricated samples with 1.6µm in diameter and 3.6µm in periodicity and 50nm gold layer thickness [29].

The Imaging in this study was performed using different tools such as Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM).

The SEM measurements for observing the samples were done with 3kV beam acceleration voltage. In SEM imaging electron beams are sent to the surface to perform the scanning. The incident electron beam is reflected and partially scattered once it hits the sample. The imaging is based on reflected electrons being collected by the detector. The geometry and material contrast is given by scattering and absorption respectively.

The structures which are to be used for incident light filtering purposes within the mid- and long- wave infrared range, are studied in terms of their transmission spectrum. The transmission of the fabricated samples, were characterized using Fourier Transform Infrared (FTIR) spectroscopy. The results and discussion are presented in the next chapter.

2.4 Results and discussions

The characteristics of the samples are discussed in this chapter. The results are grouped into four sub-sections based on the design parameters affecting the transmission spectra. The sub-categories are pitch size (2.3.1), fill factor (2.3.2), the metal layer thickness (2.3.3) and the choice of the substrate material (2.3.4). In order to analyze and identify the effect of each parameter on the transmission, each parameter is discussed independently of the three others.
2.4.1 Influence of pitch size

Pitch size is the periodicity of the holes in the photonic crystal structure. This is defined by the periodicity of the mask used in the photolithography step of the fabrication. In this case the outcome pitch size is one fifth of the mask structure periodicity due to the stepper magnification ratio. Figure 2.6 shows four transmission spectra of the metallic photonic crystals of different pitch sizes. The pitch sizes studied are 1.8 µm, 2.3 µm, 3.6 µm and 4.0 µm.

The photonic crystal samples chosen to be used for the transmission spectra presented in Figure 2.6 were all fabricated on silicon substrate with a 100nm patterned gold film on top. The fill factor (section 2.3.2) of all four samples was 73% of the surface.

![Figure 2.6: The transmission spectra curves of samples with pitch sizes of 1.8µm, 2.3µm, 3.6µm and 4.0µm. λ₁₀ and λ₁₁ refer to the fundamental mode and higher order mode respectively [29].](image)

The wavelength referring to the fundamental mode (first harmonic) and the higher order mode (second harmonic) of each of the pitch sizes are listed in Table 2. It can be seen that the wavelengths linearly change as the pitch size is
changed in the fabricated samples. For comparison the surface plasmon resonance wavelength data is calculated with Equation 2.2 [38,40] and is also presented in Table 2.

\[
\lambda_{ij} = \frac{p}{\sqrt{i^2 + j^2}} \text{Re} \left\{ \left[ \frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d} \right]^{\frac{1}{2}} \right\}. \\
(2.2)
\]

\( p \) is the pitch size of the periodic structure. \( \varepsilon_m \) and \( \varepsilon_d \) are the dielectric constants of the metal and dielectric (in this case the semiconductor substrate) respectively. \( i \) represents the x direction and \( j \) the y direction in the 2-D spatial coordination which also specify the orders of the harmonics. The substrate for the samples presented in Figure 2.6 is silicon with dielectric constant of 11.9 in this wavelength range, which is negligible in comparison with the very high real part of the dielectric constant of \( \text{Au} \).

\[
\text{Table2: The first- and second- order resonant wavelengths of the fabricated pitches calculated and experimentally measured [29].}
\]

<table>
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<th>Pitch (µm)</th>
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<th>( j=0 )</th>
<th>( i=1 )</th>
<th>( j=1 )</th>
<th>( i=1 )</th>
<th>( j=0 )</th>
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</tr>
<tr>
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<td>5.6</td>
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<td>1.8</td>
<td>6.2</td>
<td>4.4</td>
<td>6.2</td>
<td>4.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.4.2 Influence of fill factor

The fill factor refers to the hole area coverage of the surface of the fabricated samples. The calculation of the fill factor relation can be found in Equation 2.3, where \( d \) is the hole diameter and \( p \) is the pitch size.

\[
f = \frac{\pi}{4} \left( \frac{d}{p} \right)^2 \\
(2.3)
\]
The different fill factors are achieved by varying the etching time. The longer the etching time, the higher the fill factor would become. Figure 2.7 demonstrates a group of samples all with the same Au layer thickness (100nm) with the same pitch size and substrate material which were etched for different times to study the fill factor effect on the transmission spectra. Figure 2.7 (a) shows the group of samples on Si substrate and pitch size of 3.6 µm and Figure 2.7 (b) is the set of samples fabricated on the GaAs substrate with 4.0µm periodicity constant of the etched holes.

Figure 2.7: The transmission spectra of metallic photonic crystals etched into 100 nm Au film with different hole diameters on (a) Si – pitch size of 3.6 µm and (b) GaAs substrate – pitch size of 4.0 µm [29].
As it can be seen in Figure 2.7 the surface plasmon resonance wavelength peak is kept constant despite varying the hole sizes. However the curves peak changes in transmission amplitude and bandwidth. The bandwidth and the maximum transmission increase as the fill factor increases.

As the ultimate goal of this structure is to be integrated onto a detector, in this section it was shown that the corresponding wavelength of the transmission peak should be defined by specifying the pitch size of the structure. As for the specifications of the peak transmittance, the tradeoff between the bandwidth (affecting the Q factor) and the transmission amplitude should be considered. If the integrated detector has a specific tolerance around its working wavelength, the tolerance can be considered in designing the structure in terms of the bandwidth. This in turn would restrain the maximum transmission that can be obtained from this mPhC structure. To achieve the hole size within the restraints of the tolerance the etch time and the etch rate needs to be optimized accordingly.

2.4.3 Influence of metal thickness

The etching step in the fabrication is stopped at the substrate layer since the wet etch is material-selective and only suited for etching gold. Therefore the metal layer thickness defines the hole depth of the photonic crystals. Figure 2.8 shows the transmission curves of 4 sets of samples with 4 different hole diameters all with the same pitch size of 3.6 µm fabricated on Si substrate. The hole diameters take the values of (a) 2.7 µm, (b) 2.5 µm, (c) 2.0 µm, and (d) 1.6 µm. At each hole diameter the samples share the same fill factor. Two metal film thicknesses of 100 nm and 200 nm are fabricated for each case defining two hole depth for each set.
Figure 2.8: The transmission spectra of mPhc on Si substrate with the two Au film thicknesses of 100 nm and 200 nm with hole diameters of (a) 2.7 µm, (b) 2.5 µm, (c) 2.0 µm, and (d) 1.6 µm [29]. The pitch is fixed at 3.6 µm.

As it can be seen in the curves the trend following the deeper holes in to show a higher Q factor and better wavelength selectivity (smaller bandwidth). However, as the hole diameter approaches half the pitch size, the peak tends to have even higher transmission amplitude which is not the case for bigger hole diameters. The presented curves show the flow of the trend to change once the hole diameter (1.6 µm) is smaller than half the pitch size (3.6 µm). As the final transmission spectra in Figure 2.8 (d) shows, the sample with 200 nm deep holes has a much higher transmission and high Q factor and comparable selectivity at the same time. This could be due to the fact that in PhC structures with small hole sizes the scattering losses at the fundamental mode are far less than the structure with bigger hole sizes; based on better optical in-plane confinement [41]. It is worth mentioning that the transmittance for the hole diameter 1.6 µm is less than 1% which makes the structure technically opaque in this wavelength range.
2.4.4 Influence of substrate material

The substrate material is defined by the device material when the integration is performed. Different samples were chosen to study the effect of the substrate material on the transmission spectra of the structure fabricated. Here are two sets of samples showcased in Figure 2.9. The sample in each set have the same hole diameter and consequently the same fill factor; i.e. (a) 2.2 µm and (b) 2.4 µm. The photonic crystals of both sets have a pitch size of 4.0 µm and are patterned into 100nm gold film. As the samples vary in substrate material, the dielectric constant $\varepsilon_d$ in Equation 2.2 which was previously used for defining the surface plasmon resonance wavelength changes. GaAs and silicon have dielectric constants of 10.9 and 11.9 respectively. As shown in Figure 2.9 this introduces a blue shift in the transmission curves.

![Figure 2.9: The transmission spectra of the samples on 2 different substrates of Si and GaAs with hole diameter of (a) 2.2 µm and (b) 2.4 µm with gold film thickness of 100 nm [29].](image)

The choice of GaAs was due to its popularity for IR detectors’ base material. This is based on GaAs transparency within the mid wave IR (MWIR) and long wave IR (LWIR).

2.5 Conclusion

Through the process suggested in this chapter, the metallic photonic crystal structure design parameters affecting the transmission spectra have been identified and further studied. This was done for the purpose of future integration into IR photodetectors.
It was found that the position of the transmission spectrum bandpass was strongly related to the hole pitch, that is the distance between holes in the photonic crystal structure. A smaller pitch shifts the pass bands to smaller wavelengths. In the example studied with a fixed 73% fill factor in gold on a silicon substrate one micrometer change in pitch size accounted for a transmission wavelength shift of about 4.6µm. The fill factor or hole diameter parameter will, with other parameters fixed, affect absolute transmittance. A higher fill factor will by itself increase transmittance, but it will also affect how hole depth or crystal structure thickness behaves. For a fixed fill factor, changing the hole depth will have little effect on the transmission spectrum, but for a higher fill factor a increased hole depth will lower transmittance but narrow the transmission peak. For a lower fill factor, a deeper hole depth will instead increase both transmittance and narrow the transmission peak. Material choice is primarily defined by the bulk material on which the detector is based on and seems to have a smaller influence in transmission peak shift.

It remains to perform integration of the photonic crystal structure on top of a QDIP array and explore the compatibility and performance advances made by the integration.
Chapter 3

Double resonator transparent conductor

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The chapter proposes a new structure to replace ITO as a transparent conductor. After a short overview on transparent conductors in 3.1, the design of the double resonator structure suggested to replace ITO is presented in 3.2 including the transfer matrix method and the examples of the resonator structure. The specification of the fabrication and optical measurement setup are presented in section 3.3 and 3.4 respectively. Then the results of the optical measurement including the angle- and polarization-dependent transmission spectra of the samples are further demonstrated and compared with the simulated results in section 3.5. The electrical characteristics of the structure are presented in section 3.6. The final section is a brief conclusion (3.7) regarding the evaluation of the proposed structures for replacing of ITO in the transparent conductor optoelectronic applications.

3.1 Overview on transparent conductors

Transparent conductors are passive structures transparent in a specified wavelength range (within the visible or near infrared range) while showing a good electrical conductivity. The optical transparency promotes them as a proper choice for capping the light filtering window covering device's active layers beneath. Being electrically conductive is an essential property for serving the purpose of electrodes and electrical connections to the structure composed of the active material. Materials being electrically conductive and optically transparent are necessary for many optoelectronic devices, such as displays, smart windows, Vertical Cavity Surface Emitting Lasers (VCSEL) and light emitting diodes (LEDs) [42-46]. So altogether the diverse applications of transparent conductors have made them a hot research topic.

Indium tin oxide (ITO) is one of the most prominent transparent conductive oxides (TCO) due to its good electrical conductivity and transparency [47].
However the limited access to indium has made ITO a relatively expensive material to use in industry. In spite of the price issues, brittleness of ITO has also motivated many researches to be done on replacing ITO in transparent conductive electrodes (TCEs).

Several possible replacements for ITO have been revealed so far. The debate on the proper replacement has been between options such as percolated carbon nanotubes [43,48,49], conductive polymers such as Poly(3,4-ethylenedioxythiophene) (PEDOT) [50-51], and graphene [52,53]. Another explored option is using noble metals film (which often has a conductivity value better than ITO) as a basis for replacing ITO. However in order to achieve the transparency comparable to that of ITO these metallic film should be nano-engineered [54-58]. One way is to pattern the surface either by lithography techniques [54,55] or random patterning through weaving [56, 59,60]. The instant issue emerging for replacing ITO with these products is the fabrication difficulties which in turn increases their price for industrial applications as well as not achieving as good as transmittance as ITO.

The possibility to replace ITO with a double resonator composed of multilayer stack of metal and dielectric was investigated [61]. The multilayer structure filters light by following the principle of “optical cavity”. One of the most attractive advantages of this double resonator is the potential for mass production for industrial and commercial devices [62]. This is due to the well developed technology of metal deposition which makes the fabrication of very thin film metal layers with good uniformity, reproducibility and accuracy possible. Another advantage of using noble metals is their high electrical conductivity.

3.2 Design

In this section the design of the double resonator structure is discussed. First the general concept of double resonators for the purpose of transparent conductors is introduced. Then the calculation method and finally some examples of resonator structures are presented.
Figure 3.1: Schematic of the structure made up of two back to back resonators including the glass substrate and the capping layers. The film thicknesses in this schematic are not to be taken literally compared to the thicknesses designed and fabricated [61].

The proposed structure shown in Figure 3.1 is made up of two back to back metal-insulator-metal resonators (double MIM resonator) with identical layer thicknesses. Selective transmission of light in this structure is based on the working principle of a single resonator forming a cavity (in this case within the visible and near infrared wavelength range) and the interaction between layers of thin films stacked together. Each single resonator of this structure is a metal-insulator-metal (MIM) resonator [63,64] in which the thickness of the spacer dielectric layer determines where the cavity mode resonance peak stands. One resonator takes the role of the light receiver and the other is the light transmitter. This coupling is best reached when the two resonators have the same resonance frequency meaning that they are identical in layer thicknesses. The thickness and optical properties of the materials in the layers of the structure can be chosen in order to achieve the desired transmittance or reflectance window. The thickness of the middle metal layer controls the coupling between the two resonator modules [65]. In addition to the coupling, the role of the metal layer is specifically important due to its good electrical conductivity. The metal layers have to be sufficiently thin, in the order of the metal’s skin depth, to avoid high absorption and therefore opaque structure. At the same time they should be thick enough to facilitate the desired electrical conductivity. The filtering effect at visible range together with the conductivity
of the proposed structure makes it a good replacement for the ITO as a transparent conductor. Calculating the transmission window reached by the proposed double resonator structure is calculated by the transfer matrix method (TMM) [63,66-70].

The proposed structure is a stack of layers each having a certain refractive index and thickness. All layers are planes perpendicular to a virtually chosen fixed direction. Assuming that each layer is an isotropic and homogeneous medium with constant properties throughout its plane, light propagation can be defined by a linear 2x2 matrix which is called a transfer matrix. The medium where light enters the stack of layers with the $\theta$ angle of incidence is the same as the exit medium (air in this work).

There are two group of matrices used for defining the transfer matrix of the whole structure. The first is the propagation transfer matrix within the $j$-th layer as given by Equation 3.1.

$$M_j = \begin{bmatrix} e^{i\beta_j} & 0 \\ 0 & e^{-i\beta_j} \end{bmatrix} \quad (3.1)$$

where $\beta_j$ is given by Equation 3.2. Here $\beta_j$ is the phase shift introduced by layer $j$ with $d$ thickness and $n_j$ refractive index at light with $\lambda$ wavelength entering the medium with $\theta$ angle of incidence.

$$\beta_j = 2\pi \left( \frac{d_j}{\lambda} \right) n_j \cos \theta \quad (3.2)$$

The second group of matrices used for the TMM is the interface matrices defining the light propagation in the media interfaces between the adjacent layers of $j-1$ and $j$ as given by Equation 3.3. In this equation $r_j$ and $t_j$ are the interface reflection and transmission Fresnel coefficients respectively.

$$I_{(j-1)j} = \begin{bmatrix} 1 & r_j \\ t_j & 1 \end{bmatrix} \quad (3.3)$$

The plane wave traveling through the structure in plane $z$ defined by $E(z)$ is given by Equation 3.4. $E^+(z)$ and $E^-(z)$ are the complex amplitudes of the forward and backward propagating plane wave.
\[ E(z) = \begin{bmatrix} E^+(z) \\ E^-(z) \end{bmatrix} \quad (3.4) \]

Taking into account two parallel planes of \( z' \) and \( z'' \), the wave transferred from one to another can be defined as in Equation 3.5.

\[ E(z') = SE(z'') \quad (3.5) \]

where \( S \) is the transfer matrix of the whole structure with \( N \) different layers positioned in medium 0, presented in Equation 3.6.

\[ S = I_{01}M_1I_{12}M_2 \ldots I_{(j-1)j}M_jI_{j(j+1)} \ldots I_{(N-1)N}M_NI_{N0} = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} \quad (3.6) \]

Taking air as the 0th medium, the wave transferring through the stack of layers can be simplified into the following multiplication of matrices using the transfer matrix:

\[
\begin{bmatrix} E^+_0 \\ E^-_0 \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} \begin{bmatrix} E^+_0 \\ 0 \end{bmatrix} \quad (3.7)
\]

The Transmission, \( T \), of the full structure can then be defined as followed:

\[ T = \left| \frac{E^+_0}{E^+_0} \right|^2 = \left| \frac{1}{S_{11}} \right|^2 \quad (3.8) \]

As seen by Equation 3.2, the design parameters for the propagation of the wave in the structure are governed by the product of the materials wavelength specific refractive index and film thickness. In this thesis, gold and silver were used as the choice of noble metal layers. Their optical constants can be found in Figure 3.2. These figures were extracted from data presented Johnsson and Christy [71].
Figure 3.2: (a) Optical constants of Silver. (b) Optical constants of Gold.

Figure 3.3 (a) demonstrates the transmission spectrum of the multi resonators differing in the number of the combined resonators varying from single resonator system, to a dual and a triplet system in series. The series of multi-resonator structures are made by the MIM structures sharing the side metal layers met by the other MIM structure. For example the dual-resonator structure would be a metal-insulator-metal-insulator-metal structure and in this case Ag/Al₂O₃/Ag/Al₂O₃/Ag. Observing the three shows the tradeoff between the bandwidth, amplitude. Another parameter to take into account for choosing the number of the resonators is the growing product fabrication price with the increase in resonators number. The dashed curves in Figure 3.3(a) are the absorption spectra of the structures. It can be seen that the absorption increases with increase of the multiplicity of the resonator that is due to the absorption of light in metal layers.
The effect of changing the middle silver-layer thickness $d_2$ on the double-resonator’s transmission spectrum is shown in Figure 3.3 (b), calculated also with TMM. When the middle silver layer is very thick (>60 nm), the whole structure is opaque. As the thickness decreases, the overall spectrum exhibits one transmission band, resembling that of a single resonator case owing to very weak cavity coupling; then the band splits into two and the splitting is increasing owing to stronger and stronger cavity coupling.
The investigated structure is meant for integration to the LED and to deliver the highest transparency possible within the desired wavelength of 550 nm – 650 nm. The simulations for the visible range were first carried out for samples based on silver and aluminum oxide stack of layers prior to fabrication. The following are optimized thicknesses from the simulation the structure is based on: Al₂O₃: 108 nm, Ag: 10 nm, Al₂O₃: 130 nm, Ag: 25 nm, Al₂O₃: 130 nm, Ag: 10 nm, Al₂O₃: 108 nm.

3.3 Fabrication methodology

The double resonator was made by depositing stacks of Al₂O₃ with Ag or Au on top of a highly transparent and colorless 400 µm glass substrate with a dimension of 2.2x2.2 cm². After an organic contaminate clean the sample was processed in an electron-beam evaporation chamber capable of depositing metals and dielectrics without breaking vacuum. This allows the creating of a good interface which is critical for the function of the resonator structure. The deposition tool (Provac PAK600) was operated at a pressure of 5x10⁻⁷ mbar and with deposition rates of 1Å/s for all of the materials.

When compared to the metallic photonic crystal described in chapter 2, the necessary precision and control of this metal layer was much more critical, and the choice of deposition technique became very critical. The electron-beam physical vapor deposition (EB-PVD) technique is a thin film deposition process used to deposit sensitive and difficult to deposit (through other deposition methods) materials with a very high precision and control. Its strengths compared to other comparable techniques such as CVD or sputtering is its high material utilization efficiency, low temperature yet still high deposition rate. The operating pressure of the EBPVD process is typically in the area of 10⁻⁷mbar so that a high energy electron-beam can be directed towards the deposition material.

The deposition material is either a small ingot or rod stored in a cooled crucible which is then bombarded by the electron-beam. The high energy transferred into the deposition material will sublimate the material which will, in the long mean-free-path chamber, move in an arc towards the target substrate of the process. When the material reaches its target it will reform on the surface, and the strength of diffusion with the interface is dependent on
the interface of the target substrate, the energy of the deposition material as well as the substrate temperature. A higher deposition energy as well as substrate temperature will increase chemical interactions between the deposited material and the substrate.

Multiple calibration runs were performed to make sure that the correct thicknesses would be deposited in a single run without opening the chamber. After deposition a sample on silicon substrate was cleaved and examined using scanning-electron microscopy (SEM). A calibration of the deposition rate and quality was performed following each run by the SEM of the cleaved sample cross section. A sub-micrometer resolution could be achieved and the film thicknesses could be qualitatively verified, as can be seen in Figure 3.4 (a) and (b). The sample shown was deposited in the following order: $\text{Al}_2\text{O}_3$: 108 nm, Ag: 10 nm, $\text{Al}_2\text{O}_3$: 130 nm, Ag: 25 nm, $\text{Al}_2\text{O}_3$: 130 nm, Ag: 10 nm, $\text{Al}_2\text{O}_3$: 108 nm.

As can be seen in Figure 3.4 (c) the metal layer was quite grainy and coarse but as will be discussed later the results were still satisfactory. A very important factor would be the transparency of the multilayer structure and as can be seen in 2 (d) where a double-resonator structure on a glass substrate is shown on top of a sheet of paper the transparency is still quite good with the total of 45 nm of silver in the resonator layers.
3.4 Optical experimental setup

Measuring the transmission spectrum of the sample was performed using a visible and near-infrared home-made spectroscopy measurement setup as shown in Figure 3.5. The light comes from two light sources, deuterium and halogen lamps, going through a collimator. As specified by the diaphragm the illuminated light has a 5mm diameter spot size. Once transmitted through the polarizer (when doing the TM and TE measurements) the light hits the sample. The transmitted light through the sample is then collected by fiber and sent to the optical spectrum analyzer (OSA). The measurement setup is shown in Figure 3.5.

Figure 3.5: The measurement setup with polarizer.
3.5 Results and discussions

3.5.1 Silver resonator

The schematic structure of the silver resonator based on silver and aluminum oxide mix of MIM resonators is previously shown in Figure 3.1. The transmission measurements done were both angle- and polarization-dependent which are presented in Figure 3.6 (the curves on the left; a and c) together with the corresponding simulation results (the curves on the right; b and d) done prior to the fabrication. The two top curves are the TM spectra and the two bottom curves are the TE transmission spectra. The cover glass substrate is taken into account in all the angle- and polarization- dependent simulations. In order to smoothen the curves which turn out very noisy due to the interference caused by including the substrate in the simulation, the moving average algorithm is used. The integration is done over a 30 nm spectral range. The maximum transmission reached by this structure is 86% based on the simulation results. At the same time, the measurements show the maximum amplitude of the transmitted light to be 76% at normal light incidence. The bandwidth of the transmission window of the designed structure calculated by full width half maximum (FWHM) method is to reach 158 nm biased around 650 nm. The measurement however shows the fabricated sample to have a FWHM of 150 nm transmission window centered on 643 nm.

As previously mentioned the transmission through this structure is angle and polarization dependent. In order to evaluate the simulation results for the angle-dependent through different polarization a polarizer is added to the optical measurement setup. Then the sample was illuminated by different polarizations (TM and TE polarization) as the angle was varied from 0 (normal incidence) to 60 degrees. The polarization-dependent measurement setup is shown in Figure 3.6. The sample proves to be in good agreement with the simulation.

As demonstrated in Figure 3.6, in transverse magnetic (TM) measurements the amplitude of the transmission window peak turns to remain almost the same throughout the changing of the angle. The FWHM is increasing from 145 nm at 0° to 170 nm at 60°. In transverse electric (TE) measurements, the
amplitude of the peak decreases from 76% to 65% while the FWHM changes from 145 nm to 105 nm. It is also demonstrated in Figure 3.6 (a) that for a double resonator structure the transmission is enhanced by 40% (from 54% to 76%) at the normal incidence in comparison with a 10nm silver thin film. This enhanced transmission over 110nm spectral range is due to the presence of the FP cavity mode in this symmetric structure. This is in spite the fact the structure has a total of 45nm of silver film (3 layers of 10 nm – 25 nm – 10 nm) used in its stack of layers.

![Image](image)

*Figure 3.6: Angle- and polarization-resolved transmission spectra for the gold sample, (a) TM (measurement); (b) TM (simulation); (c) TE (measurement); (d) TE (simulation) [61].*

### 3.5.2 Gold resonator

Following the samples made based on silver, gold was proposed as another alternative noble metal. The Au-based double resonator sample is made up of stacked layers of Au: 11 nm; Al₂O₃: 148 nm; Au: 30 nm; Al₂O₃: 150 nm; Au: 12.5 nm on cover glass substrate, an asymmetric structure by design. The fabrication and characterization process steps were the same as previously mentioned for the silver samples. TE and TM polarized incident light with angles varying from 0 to 60 degrees using the same measurement setup
demonstrated schematically in Figure 3.7. The TM and TE mode measurement curves are presented in Figure 3.7 (a) and (c) respectively. The simulated TM and TE curves which were made prior to the fabrication are demonstrated in Figure 3.7 (b) and (d) respectively. For Au samples the cover glass substrate is also taken into account in all the angle- and polarization-dependent simulations.

The maximum transmission reached of the gold sample in the transmission window is 72% based on the simulations for both polarizations. At the same time, the fabricated sample has only a 62% maximum transmission at normal incidence in TM polarization and 58% in TE polarization. This could be due to the high absorption and lossy nature of gold in this wavelength range. As for the FWHM, the simulation shows a 154 nm window centered round 651 nm in TM polarization for normal incidence and the corresponding parameters of the fabricated sample are135 nm window centered around 670 nm. Similar to the silver sample amplitude of the transmission peak remain almost the same in the TM measurement while changing the angle. However in TE mode there is a 16% decrease in the amplitude of the peak as the angle increases to 60 degrees. The transmission window is slightly broadened in both cases (more in measurement than in simulation) as the incident angle increase in the TM mode. The TE mode peak position is shifted more considerably (by 100 nm) in the TE mode however there is not a considerable change in the FWHM window as the angle increases up to 60°. It is worth mentioning that the 11nm thick gold film has a lower transmission within the transmission window in comparison to the fabricated structure which has a total of 53.5 nm thick gold film.
Figure 3.7: Angle- and polarization-resolved transmission spectra for the gold sample. (a) TM (measurement); (b) TM (simulation); (c) TE (measurement); (d) TE (simulation).

3.6 Electrical characterization

Prior to the last step of the fabrication process, where the stack would be covered by the last layer of its Al₂O₃ capping layer, test-samples were taken out of the fabrication tool so electrical measurements could be made on the metal layer.

The figure of merit (FOM), as described by Equation 3.9, is an efficient tool for comparing transparent conductors as it effectively weighs transmittance and sheet resistance equally in measure, which can then be used to find the most efficient material or structure for a certain size.

\[
FOM = \frac{T}{R_s}
\]  

(3.9)

\(T\) is the maximum transmittance and \(R_s\) is the sheet resistance.
A comparison between the test structure as well as a novel improvement on ITO is shown in Table 3.1. Here the transmittance and sheet resistances have been measured, followed by extracting the figure of merit through taking the ratio between the maximum transmittance and sheet resistance.

Table 3.1: A comparison between the optical and electrical properties of ITO and Ag-based double resonator [54,61].

<table>
<thead>
<tr>
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<th>Transmittance</th>
<th>Sheet resistance</th>
<th>Figure of merit</th>
</tr>
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<tbody>
<tr>
<td>ITO</td>
<td>0.88</td>
<td>60</td>
<td>$1.5 \times 10^{-2}$</td>
</tr>
<tr>
<td>Ag-double resonator</td>
<td>0.79</td>
<td>7.8</td>
<td>$10 \times 10^{-2}$</td>
</tr>
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</table>

It can be seen in Table 3.1 that the silver-based multi-layer structure has a figure of merit that is nearly seven times higher than current commercial ITO films.

3.7 Conclusion

The proposed structure of double resonators has both good optical transparency and electrical conductivity (6% lower transparency but having almost 7 times higher conductivity when compared to ITO) which makes a very good candidate for replacing ITO because of the better figure of merit. The silver based metal-insulator structure with a FWHM of 150 nm and maximum transmission amplitude of 76% (normal incidence) also has a low angle-dependency in TM mode. The structure can also be fabricated without capping layers and simulation studies claim that it would yield similar results. Because of its good optical and electrical properties, this structure has great potential as a replacement solution as the transmission window can be shifted by changing the layer thicknesses, tuning it for capping specific optoelectronic devices with certain operating wavelength in their active layer. It is also important to mention its suitability for mass production and structure stability due to the materials used in this proposed structure. The multilayer structure has an inherent limitation of the transmission window being narrow. This is a disadvantage for applications concerning a broadband transmission spectrum.
The next step to prove the suitability of the double resonator structure would be to use it as the top electrode of an optical emitter. By manufacturing it on top of a simple light emitting diode in the relevant wavelength spectrum, one can test that the functionality of the LED still works as expected. It also needs to be determined if the figure of merit of the resonator structure remains better than ITO when integrated as the top electrode. When doing this, the top electrode should be designed so that both electrode alternatives give the same device resistance within limits that are suitable for the device. This will make comparisons between the two highly relevant for direct applications. Possible process complications because of post-processing after metal deposition on top of a sensitive semiconductor interface should also be investigated.
Chapter 4

Lithography-free large-area NIR absorber

The chapter proposes a nanostructured absorber in the near infrared (NIR) range. After a short overview of the metamaterial and nanostructured absorbers in part 4.1, the design of the monolayer gold nanoparticle based absorber structure is suggested in part 4.2 including an overview of work previously done in the visible range. Fabrication and optical measurement setup are presented in sections 4.3 and 4.4 respectively. Then the results of the optical measurement are further demonstrated and discussed in section 4.5. The final section (4.6) is a brief conclusion about potential applications for this structure.

4.1 Overview of metamaterials and nanostructured absorbers

Metamaterials or artificially engineered electromagnetic materials have become a fascinating research field. Nano- and micro-structured materials can exhibit certain properties superior to bulk natural materials; therefore they can be advantageous for specific applications. The possibilities presented by these artificially designed materials are abundant and versatile. The spectral responses of metamaterials are distributed over a wide range of wavelengths, from visible [72, 73] to near infrared [8, 74, 75], infrared (IR) [76, 77], and terahertz [78].

Metallic nanostructures as a popular metamaterial have been widely investigated for quite some time thanks to strong light-matter interaction in metal nanostructures. In practice forming such structures through patterning a thin layer of metal nanostructure on top of a dielectric material surface is more feasible. Such a metamaterial surface usually possesses surface plasmon resonances (SPRs), which results in strong light absorption/transmission at specific wavelengths. The responsive wavelength ranges can be designed based on metal nanostructure’s size and/or shape. Multilayer designs can also be realized; combination of metal nanostructure layer and dielectric spacer can lead to interesting interference effect, resulting in more versatile optical properties [37, 79].
The most common way of fabricating gold nanostructures is to use some lithography technique. Electron-beam lithography [8,74], nanoimprint [9], semi-continuous metal films [80], metal nanoparticles [81], nano-spheres [82] or self-assembly techniques [83,84] are used depending on the targeted wavelength range concerned.

Another way to fabricate a nanostructured metallic layer is to form gold clusters by heating a thin gold film coating to a relatively high temperature, which can be significantly below bulk gold melting temperature [72]. At a certain temperature gold softens, and the surface tension breaks the film into clusters. This irreversible process is temperature dependent. Another parameter affecting the agglomeration outcome is the film thickness.

Such a mono-layer of gold nanoparticle can be easily integrated into a multilayer structure. Especially when it is placed on top of a metal reflector, separated by a dielectric spacer, this mono-layer of gold nanoparticles can help to achieve strong light absorption. Such composite multi-layer structure of an ultrathin thickness can be used for large-size low-cost solar cells or spectrally selective solar absorber [85]. Previously we made samples for absorbing visible light [72]; here we geometrically optimize the fabrication parameters and achieve light absorption at NIR wavelength range.

4.2 Design

First the general concept of gold nanoparticle monolayer for the purpose of absorption is introduced based on the previously done work in [72]. Then the specifications of the fabricated samples are presented.

Figure 4.1: Schematic of the structure before thermal annealing [86].
The proposed structure before thermal annealing (Figure 4.1) is made of a single resonator on top of a one-side polished silicon wafer as the substrate. The resonator is composed of two metallic layers: a thin gold layer on top as the absorbing layer; and a comparatively thick 100nm aluminum layer at the bottom as the reflector. The two metal layers are separated by a middle aluminum oxide layer, which is the dielectric spacer in the structure.

The cleaved samples are thermally annealed in a range from 350º C to 450º C. The resulted samples have a discontinuous top gold layer. The islands formed on the top are different in size, thickness and distribution. These parameters are decided by the thickness of the top gold layer, the annealing temperature and the annealing duration. The schematic of the resulted samples are shown in Figure 4.2.

The SEM images of the top view of a set of chosen samples are shown in Figure 4.3. The SEM images demonstrate a trend of how annealing affects the top gold layer agglomeration. All three presented samples are primarily composed of silicon substrate with 100 nm of aluminum reflector layer coated with 110nm aluminum oxide spacer and 21 nm of Au and they have all been through the same fabrication and annealing procedure except for their annealing temperature which varies from 350º C to 450º C. As it can be seen in the SEM images the metal thin film is already broken at the 350º C and clearly defined clusters start getting shaped at 400º C. And at 450º C the gold islands are fully formed and detached from one another. Ultimately the minimum specular reflectance dip was obtained from the sample annealed at
$450^\circ C$ in which the metal island formation is completed as can be seen in Figure 4.4. Taking into account that the scale bar in the SEM images is 1 $\mu$m, it can be seen that the gold islands formed have random sizes up to a few hundred nanometers.

The four samples presented in the photograph Fig. 4.3 (d) are the pre-annealing sample (top right), $450^\circ C$ annealed sample (top left), gold-coated Si substrate (bottom right), aluminum-coated Si substrate (bottom left). The SEM images of the samples annealed to $350^\circ C$, $400^\circ C$, $450^\circ C$ are demonstrated in Fig. 4.3 (a), (b) and (c) respectively.

![Figure 4.3: Top view SEM images of samples with 21 nm top Au layer annealed at (a) $T=350^\circ C$, (b) $T=400^\circ C$ and (c) $T=450^\circ C$. The scale bar is 1 $\mu$m. (d) Top row shows 21 nm top Au structure annealed at $450^\circ C$ before (right) and after (left) anneal. Bottom row shows the aluminum (left) and gold films deposited on silicon substrates separately [86].](image)

Based on Fourier-transform infrared (FTIR) measurements of the samples, the ones where the islands are separated with well-defined boundaries have a lower specular reflectance. The metal-island film forming a plasmonic nanostructure is coupled through the dielectric spacer with the reflecting metallic mirror. Their collective response leads to a high-performance light absorber. The mechanisms responsible for high absorptivity of this nanostructured multilayer include plasmonic dipole resonance of the gold islands, coupling of the dipoles, as well as coupling of light to surface-plasmon polariton guided by the reflector-spacer interface [72]. The high electric field intensity at the sample's surface can also be potentially used for
nonlinear optics applications.

In order to further study the effect of geometry on absorption band, a number of samples with different top gold layer and various spacer thicknesses were fabricated and annealed.

4.3 Fabrication methodology

Here the fabrication methodology of the samples is presented. Single-sided polished silicon wafers are used as substrate material. The fabrication process was started with deposition of 100 nm of aluminum through the use of an electron beam evaporation system. The deposition pressure is 5x10⁻⁷ mbar. After this an atomic layer deposition (ALD) system is used to create a highly controlled aluminum oxide layer with an accuracy of less than a nanometer. The thicknesses fabricated vary from 80 nm to 194 nm based on the structure design. The relatively high refractive index of alumina and its stable processing properties are perfectly matched for this fabrication technique. The oxide layer is then covered with a comparatively thin controlled evaporated gold film. The samples were fabricated in 3 batches of 15 nm, 21 nm and 27 nm top gold layer. This layer is deposited with a constant rate of 2 Å/s using thermal evaporation method under the pressure of 5x10⁻⁶ mbar. The unwavering optical characteristics of gold thin film / islands when exposed to atmosphere and annealed to the melting temperature, make it the suitable metal for this study.

The samples are then cleaved into 2x2 cm² pieces and subsequently annealed in an oven in atmospheric ambient. The annealing temperatures range from 350° C– 450° C. The target temperature was reached in about 30 minutes. The samples were kept in the heated oven for approximately 20 more minutes before the oven was turned off. During this time period the temperature in the oven reached a 70° C overshoot in every case before automatically lowering the temperature back to the target temperature. The samples were taken out of the oven to the ambient temperature in about 50 minutes when the chamber temperature has reached 125° C in the cooling process.
4.4 Optical measurement setup

In this section the optical measurement setup which is used for the fabricated samples are introduced. Due to limitations imposed by the detectors and beam splitters available, two measurement setups were used for the characterization of the fabricated samples. From 500 nm – 950 nm the measurements were done by a home-made spectroscopy measurement setup composed of a light sources (deuterium and halogen lamps) a silicon based detector and an optical spectrum analyzer. From 950 nm – 3 µm the samples were characterized by VERTEX 70v, which is a FTIR spectroscopy tool by Bruker. The tool is composed of a NIR light source, a KBR broadband beamsplitter, and the ultra-wide range room temperature DLaTGS detector.

4.5 Results and discussion

In this section the optical measurement results achieved using the presented setup are demonstrated and further discussed. Firstly in 4.5.1 the specular reflectance measurement results are demonstrated and then in 4.5.2 these results are compared to the diffuse reflectance measurements made on two of the chosen samples.

4.5.1 Specular reflectance measurement results

Once annealed, the fabricated samples are expected to have an absorption bandwidth due to the plasmon resonance of the gold dipoles and the surface plasmon polaritons (SPP) excited through top random nanoparticles and the bottom interface of spacer dioxide and reflector. The preliminary reflector follows the Fabry-Pérot resonance mechanism ruling the metal-insulator-metal structure. However, as shown in Figure 4.4, annealing transforms the multilayer reflector into a perfect broadband absorber. All the specular reflectance measurements were done at the incident angle of 10 degrees. The dashed line in the graph below represents the simulated specular reflectance spectra of the multilayer structure before annealing. The enhanced specular reflectance curve could be due to perfect smooth surface assumption made in the calculation vs. the fabricated samples film surface.
Figure 4.4: The specular reflectance spectrum of the sample with 21 nm top gold layer, 110 nm of alumina spacer, 100 nm aluminum reflector on silicon substrate before (blue) and after (red) annealing at 450ºC. The dashed line corresponds to the simulated structure before annealing [86].

These multilayers’ optical characterizations are closely related to the two major elements of spacer thickness and top gold layer thickness. The fabricated samples have a broad band of low specular reflection as shown in Figure 4.5. The figure demonstrates that in the spectra from different samples, the maximum specular reflectance varies as the spacer thickness changes. The effect is, however, not linearly correlated to the spacer thickness. The optimum aluminum oxide thickness for this structure is 110 nm, which results in a minimum of 2% specular reflectance. Both increasing and decreasing the oxide layer thickness decreases the absorption of the structure. The origin of this high absorption stems from the interband transition of gold. All these samples are annealed at 450ºC under the same conditions and they all have 21 nm top gold layer.
Another parameter affecting the SPP is the top gold layer thickness. The effect is clearly demonstrated in Figure 4.6 where a slight red-shift of the minima is observed as the top gold layer gets thicker. Decrease in the specular reflection is the result of the thicker top gold layer producing on average bigger gold islands when agglomerated through annealing at the same temperature. All samples used are annealed to 450°C under the same conditions and they all have 110 nm alumina spacer layer.
4.5.2 Specular vs. diffuse reflectance spectrum

In order to further study the samples and their potential applications, two different reflectance measurements were performed on two chosen samples before drawing the conclusion of high absorption to be the dominant basis of the super low specular reflectance. This was necessary since the gold islands on the spacer surface are micrometer sized and are thus big enough to have an obvious scattering effect, causing the structure to demonstrate a noticeable amount of diffuse reflectance. In order to measure the diffuse reflectance of the chosen samples, their total reflectance was measured using integrating sphere reflectance measurements. Subtracting the two available measurements of total and specular reflectance drew the diffuse reflectance curves of the samples. The two samples chosen both have 110 nm alumina spacer layer and 100 nm aluminum reflecting layer and were annealed to 450°C under the same conditions previously described.

The specular versus diffuse reflection characterization of two of the fabricated samples are shown in the following Figures 4.7, 4.8.
Figure 4.7: Specular, diffuse and total reflectance of the sample with pre-annealing multilayer structure of 27 nm top gold layer and 100 nm alumina spacer and 100 nm aluminum reflector layer. The sample was annealed to 450°C [86].

The top gold layer of the annealed samples is 27 nm and 21 nm respectively. These two samples demonstrate very similar amplitude of specular reflectance but measuring the total reflectance draws a clear line between the absorption characteristics of the two. As the sample with 27 nm shows relatively low
diffuse reflection (maximum diffuse reflection of \(~30\%\) at approximately 1.5 \(\mu m\)) as well and therefore the absorption is much stronger than the sample with top gold layer of 21 nm (maximum diffuse reflection of more than 60\% at approximately 1.2 \(\mu m\)) where the diffuse reflection is comparably much higher. This suggests that the former with thicker top gold film and hence on average bigger gold islands is a better option for applications where high absorption in NIR is the target.

### 4.6 Conclusion

The proposed multilayer made up of a reflecting mirror layer separated by a spacer layer from the top single layer of randomly distributed gold islands was suggested and proven to have potential applicability to be used an absorber in the NIR range. Lithography free fabrication method of these structures makes them cost-efficient in comparison with other fabrication methods and applicable for large area applications. The structure showed tunable optical characteristics in the experimented range by tailoring the layer thicknesses and annealing temperatures accordingly. So far the absorption of more than 70\% over a broadband of 800 nm (at least) was shown achievable by annealing the structure with 27 nm top gold layer and 110 nm alumina spacer up to 450° C. This super thin structure (~240 nm) could be used for the purpose of solar cells. The scattering characteristics can potentially be put into use in advantage of the solar cell design setting as well.
Chapter 5

Structure-induced color formation

The chapter proposes a single resonator structure for forming continuous spectra of colors. After a short overview on visual colors in 5.1, the geometry and simulation of the reflector structure suggested are presented under the section of Design in 5.2. The fabrication methodology is explained in section 5.3. The optical measurement setup and the characterization results are presented in 5.4. In the end a brief conclusion is drawn in 5.5 to wrap the chapter.

5.1 Overview of visual colors

The phenomenon that leads to color perception is strongly linked to selective reflection and scattering as well as to absorption of certain light spectrum in the visible range. This is true both for light being transmitted through a material as well as reflected off a material. In the common process of color perception the electromagnetic radiation is absorbed through electron excitation, leading to a thermal energy conversion. Conventional coloring is based on the application of pigments or dyes to a material or surface, changing or adding to its absorbing nature in the visible range. While this technique has existed for thousands of years, man-made synthetic coloring did not come into use until the 19th century [87].

There has been an increased demand of coloring materials with increased wear and degradation resistance, production reproducibility and more distinctly unabsorbed light spectrum. These are areas where the use of conventional dyes and pigments are getting limited. Research has been done to use novel metamaterial solutions [10,11] such as plasmonic nanostructures to be used instead as the solid-state nature make such structures inherently well suited for applications with the above-mentioned demands. While the area of plasmonic nanostructures have yielded a lot of interesting results especially when it comes to the ability to distinctly transmitted or reflected color spectrum, their complicated and expensive nanofabrication restricts their possible application areas from a cost perspective. This can typically come
from a need of structure resolution of less than micron size, needing advanced and expensive lithographic or deposition techniques. [72,88-91]

Here a different solution has been proposed as an alternative, through the use of electromagnetic resonances, it has been shown that distinctly tuned color absorption can be achieved. These optical resonance structures will create an optical cavity where trapped light will dissipate as thermal energy. The spectrum of radiation trapped in the optical cavity is depending on geometric as well as material properties. This lets very specific tuning to be made through changes in structure parameters such as film thicknesses as well as material choice. These structures do not rely on plasmonic structures; because of this it does not need sub-micrometer patterning which in turn decreases processing complexity significantly. This work will in fact focus on simple continuous film structures.

5.2 Design

In this section the geometric design of the resonance structure is discussed. After this follows a presentation of a simulation performed in order to predict the behavior of the structure and a short discussion of its results. The specifications of the fabricated samples are demonstrated in Figure 5.1.

Figure 5.1: (a) Schematic of the resonator structure. 100 nm of alumina was deposited on top of a bulk silicon wafer. A gradient film between 0nm and 230 nm of alumina-oxide was deposited on
The proposed structure, as seen in figure above, is made up of a single resonator on top of a single-side polished silicon wafer as the substrate. The resonator is composed of two metallic layers; a thin 7.5 nm titanium layer on top and a comparatively thick 100 nm aluminum layer at the bottom operating as a near-perfect reflector. The two metal layers are separated by a middle aluminum oxide layer, which is the dielectric spacer of the structure. This dielectric layer is gradient varying from 0 nm - 230 nm. It is known that resonance and eventual absorption spectrum will change with spacer thickness, and so the spacer will be changed in thickness to show that the technique can be used to in a simple way control the reflected color spectrum. Because the design is now directly linked to very few parameters, it will be easier to control the reproducibility and color spectrum reflection through the thickness of only three layers.

The reflection spectrum of this single resonator structure was simulated using the transfer-matrix method used previously to simulate other resonance structures [63]. Material parameters for the alumina, aluminum oxide and titanium were referenced from different tabulated sources [71,93,94]. This simulation method does not take into account material and interface imperfections, whose consequences will be discussed later. In the simulation spacer thickness values was similarly chosen to vary from 0nm to 230nm so that the simulation could be directly compared to the experimental measurements. The simulated reflectance spectrum can be seen in Figure 5.2 and clearly shows promising characteristics for using the structure to distinctly control the reflected color spectrum. The first absorption band emerges with increasing spacer thickness and widens considerably and almost blackens the whole visible spectrum before a second reflectance band appears in the lower wavelength region. The absorption bands are not proportional in appearance in the spectral range and more will appear with higher thicknesses.
5.3 Fabrication methodology

Here the fabrication methodology of the fabricated sample is presented. All the deposition steps are performed under the chamber pressure of $5 \times 10^{-7}$ mbar using an electron-beam evaporation system. Single-side polished silicon wafers were used as substrate material. The fabrication process is done in three steps. It starts with depositing 100 nm of aluminum, serving as a near-perfect reflector of the resonance structure. In the second round 230 nm of aluminum oxide was deposited as the low-loss dielectric spacer. In this step the sample is partially covered with a shield in order to facilitate a gradient change of the spacer thickness in the structure. The schematic of the sample loading setup is shown in Figure 5.3. As the last step of the fabrication the structure is covered with a 7.5 nm thick layer of titanium. This is the resonance structure’s most critical part as it is the combined light transmittance as well as absorbance layer. The semi-reflecting characteristic of the titanium is what creates the resonance effect. The titanium layer is deposited at a constant rate of 0.5 Å/s to be able to achieve the thickness specification with a good reliability. The two other layers were deposited with the deposition rate of 1 Å/s.
As mentioned the fabrication of the alumina layer with its thickness gradually decreasing is done using a shielding technique. In this method, the shield is assumed infinitely extended in the direction perpendicular to that of the sample. The shield is present to prevent the homogeneous deposition of the alumina vapor in the vacuum chamber. In practice a physical shield larger than the sample was mounted in place partially covering the sample when depositing the dielectric aluminum oxide. Because of the ballistic transport characteristics of the deposition method, this means that only the diffused molecules would deposit underneath the shielded area of the wafer. It was assumed and seen in the later results that the deposition gradient will be approximately linear. This creates a structure of 100 nm aluminum, 230 nm aluminum oxide and 7.5 nm titanium that decreases down to 100 nm aluminum, 0 nm aluminum oxide and 7.5 nm titanium at the very edge of the sample wafer. A picture of the final structure can be seen in Figure 5.1, where the gradient with spacer thickness can be clearly seen.

The sample was subsequently observed with SEM and its top view is presented in Figure 5.4. There we can see that the important top titanium layer is continuous with an average grain size of approximately 100 nm. This justifies the use of a continuous film in the design and simulation assumptions.
5.4 Optical measurement results and discussion

In this section the home-made optical spectroscopy measurement set up used for the fabricated sample is introduced. This is followed by a presentation of the characterization method and finally the results are discussed.

The setup is composed of two light sources (deuterium and halogen lamps), a silicon based detector and a spectrometer. The light source limits the possible characterization spectrum from 450 nm to 950 nm, but this covers 83% of the visible spectrum and as such will give a good indication of structures function. The spot size is 1 mm which will affect the resolution of the measurements as the resonance peaks will shift continuously with sample position.

As mentioned previously, the single resonator with the metal-insulator-metal composition follows the Fabry-Pérot resonance mechanism and therefore in essence is a selective reflector. To characterize the fabricated sample specular reflection measurements were performed at angle of incidence of 15 degrees.

The measurement starts at a point right before the reflectance spectrum changes when the measurement point moves. The next measurement is then performed consequently 1 mm towards the edge until no further change in
reflectance spectrum is recorded and the measured material is only the aluminum-titanium layer. In this measurement this took 26 recordings which give a gradient distance of 25 mm. The resulting reflectance spectrum matrix can be seen in Figure 5.5.

Starting at point 26 (or 25 mm inside the shielded area) the structure functions very much like a near-perfect mirror, as can be seen in Figure 5.5. The first absorption band appears broadly, resulting in a dark purple color before a reflecting band appear and yields a blue reflectance. In the middle of blue and yellow one would expect a green reflectance; however, there is a generally uniformly high reflectivity which leads to the color being a fully reflected gray instead of green. After this a second absorption band arrives from the lower wavelengths, leading to yellow and red being visible. A third reflection band can be seen reflecting low wavelengths at the thickest deposited structure.

![Figure 5.5: The measured reflectance spectrum of the gradient resonant structure. Every measurement point except the edge points are measurements of a gradient structure which is assumed to affect the measured resolution [92].](image)
A comparison between simulated and measured results are shown in the Figure 5.6. The red line in the graph represents the experimental data of the 46 nm spacer resonance structure and the black line the simulated reflectance spectra of the resonance structure with a 74 nm spacer. The 46 nm experimental result is the highest measured absorption peak, while the 74 nm simulation result is the highest simulated absorption. The very high absorption at 74 nm was not experimentally correlative, which could most probably be explained by the lack of resolution in the measurement, as well as the simulation result relying on perfect interfaces and no surface roughness.

5.5 Conclusion

An optical resonator cavity structure was designed, fabricated and characterized in an attempt to realize an alternative synthetic coloring material. The design uses Fabry-Pérot resonance to make it possible to create the structure with unpatterned blank metal and dielectric films, giving a large edge in fabrication cost and complexity over other similar metamaterial synthetic coloring films using plasmonic nanostructures. Experimental results show good correlation with simulation results but a loss in color saturation can be attributed partially to processing techniques that leaves slightly imperfect
interfaces and material layer. The lower color saturation of the experimental data is also largely attributed to the large measurement size of the measurement setup which measures a structure with a non-uniform spacer thickness.

The fabrication method is uncomplicated and is both distinctly tunable as well as highly repeatable. To create more defined specular reflectance spectra, higher thicknesses as well as more complicated multi-resonator structures are interesting further areas of investigation.
Chapter 6

Summary

In this final chapter the work will be briefly concluded and prospects of future work based on this thesis are drawn. This work has studied the possible uses of metal nanostructures as a way to improve performance or new possible applications of different optoelectronic devices.

The first part discusses the use of a metallic photonic crystal structure designed to improve detectivity and responsivity of quantum dot infrared photodetector in the mid and long infrared region. The design is based on surface plasmon resonance in a metal-dielectric interface. Several design parameters were investigated to find the behavior of the proposed metal photonic crystal structure, such as hole size, hole depth, fill factor and bulk material choice. All of these parameters are coupled to each other, making it important to characterize the structure’s behavior for it to be optimized in a certain region. The pitch size, or distance between the centers of holes in the metallic film, was shown to be the dominating contributor to the position of the transmission bandpass spectrum. The metallic layer thickness has an impact on the total transmittance but will have an optimal thickness for the highest wavelength selectivity. The total surface coverage of holes in the photonic crystal, or fill factor, will have an effect on the scattering and absorption in the metal layer. An increased fill factor will increase direct transmission but lower the effect of the surface plasmon resonance. Two different substrate materials were tested and showed that it does affect the transmission spectrum, meaning that the structure would need characterization and subsequent tuning after being integrated onto its host device.

The next section described the work of fabrication and characterization of a proposed thin film multilayer optical resonator. This structure was proposed as a transparent conductor capable of replacing current generations of transparent conductors through easier fabrication methods while still retaining competitive figures of merit. The conventional transparent conductor in use is Indium-Tin-Oxide (ITO). The proposed resonator structure showed a very
high figure of merit, based on conductivity in relation to optical transmission, making it competitive in performance to that of ITO. In fact at a slightly lower transmission window the conductivity of the resonator structure was sevenfold that of ITO. On top of this the fabrication complexity and material costs are lower, making it a very promising transparent conductor alternative, especially for application with smaller transmission bandwidths.

The work on the multilayer resonator gave rise to a new fabrication method that coupled to the metal-insulator photonic crystals of the first part of this thesis. Instead of using lithographic fabrication methods, which were expensive and complicated, it was proposed that a thin metallic film could be annealed in such a way that the homogenous film would be broken into a distribution of small metallic islands on top of the insulator. This was shown to be able to work well as an absorbing resonator with a specific active bandwidth within a range of 500 nm to 3 μm. Changes in metal layer thickness and anneal temperatures affected island distribution and therefore the resonators absorption spectral range. A spectral width of 800 nm was shown to have absorption of more than 70%, demonstrating promise for certain applications such as near infrared detectors.

The last part of this thesis concerns the design, fabrication and characterization of a metamaterial approach to synthetic coloring. This also includes simulation data used to tune design parameters and verify certain experimental results. The design of the metamaterial was based on a Fabry-Pérot resonator. This meant that an efficient reflector was distanced from a semi-transparent metal by a transparent insulator. The materials involved and spacer distance were crucial for the resonator behavior. Spacer distance was varied approximately linearly on a sample and consequently a range of colors was observed after the final step of the fabrication. It was shown that a range of absorption and reflection bands over a wide spectral range depend on the spacer thickness. The simulation data correlated well with the experimental results and also managed to explain certain phenomena in the experimental data such as the lack of the color green because of a too wide reflection band for that specific spacer thickness. The difference between experimental data and simulation results for spectral resolution was partially attributed to the lack of imperfect interfaces in the simulator, but also that the experimental setup was not measuring homogenous interfaces.
So far in this thesis only quantitative and theoretically drawn predictions of the impact of proposed structures for potential applications have been discussed. Ideal continued future work from this would be to integrate the proposed structures in this thesis in a chosen application and actually measure and realize the potential of them qualitatively. This would also explore the practical problems that these solutions might have when it comes to integrating them in their respective applications.
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