Surface Plasmon Hosts For Infrared Waveguides And Biosensors, And Plasmons In Gold-black Nano-structured Films

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SURFACE PLASMON HOSTS FOR INFRARED WAVEGUIDES AND BIOSENSORS, AND PLASMONS IN GOLD-BLACK NANO-STRUCTURED FILMS

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Physics in the College of Sciences at the University of Central Florida Orlando, Florida

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Major Professor: Robert E. Peale
ABSTRACT

Applications of surface plasmon polaritons (SPPs) have thus far emphasized visible and near-infrared wavelengths. Extension into the long-wave infrared (LWIR) has numerous potential advantages for biosensors and waveguides, which are explored in this work. A surface plasmon resonance (SPR) biosensor that operates deep into the infrared (3-11 µm wavelengths) is potentially capable of biomolecule recognition based on both selective binding and characteristic vibrational modes. The goal is to operate such sensors at wavelengths where biological analytes are strongly differentiated by their IR absorption spectra and where the refractive index is increased by dispersion, which will provide enhanced selectivity and sensitivity. Potentially useful IR surface plasmon resonances are investigated on lamellar gratings formed from various materials with plasma frequencies in the IR wavelength range including doped semiconductors, semimetals, and conducting polymers.

One outcome of this work has been the demonstration of a simple analytic formula for calculating the SPP absorption resonances in the angular reflectance spectra of gratings. It is demonstrated for Ag lamellar gratings in the 6-11 micron wavelength range. The recipe is semi-empirical, requiring knowledge of a surface-impedance modulation amplitude, which is found here by comparison to experiment as a function of the grating groove depth and the wavelength. The optimum groove depth for photon-to-SPP energy conversion was found by experiment and calculation to be ~10-15% of the wavelength.
Hemicylindrical prism couplers formed from Si or Ge were investigated as IR surface plasmon couplers for the biosensor application. Strong Fabry-Perot oscillations in the angular reflectance spectra for these high index materials suggest that grating couplers will be more effective for this application in the LWIR.

A variety of materials having IR plasma frequencies were investigated due to the tighter SPP mode confinement anticipated in the IR than for traditional noble metals. First doped-Si and metal silicides (Ni, Pd, Pt and Ti) were investigated due to their inherent CMOS compatibility. Rutherford backscattering spectroscopy, x-ray diffraction, scanning electron microscopy, secondary ion mass spectrometry and four point probe measurements complemented the optical characterization by ellipsometry. Calculation of propagation length and mode confinement from measured permittivities demonstrated the suitability for these materials for LWIR SPP applications.

Semimetals were also investigated since their plasma frequencies are intermediate between those of doped silicon and metal silicides. The semimetal antimony, with a plasma frequency ~80 times less than that of gold was characterized. Relevant IR surface plasmon properties, including the propagation length and penetration depths for SPP fields, were determined from optical constants measured in the LWIR. Distinct resonances due to SPP generation were observed in angular reflection spectra of Sb lamellar gratings in the wavelength range of 6 to 11 μm. Though the real part of the permittivity is positive in this range, which violates the usual condition for the existence of bound SPP modes, calculations based on experimental permittivity showed that there is little to distinguish bound from unbound SPP
modes for this material. The SPP mode decays exponentially away from the surface on both sides of the permittivity sign change.

Water is found to broaden the IR plasmon resonances significantly at 9.25 micron wavelength where aqueous extinction is large. Much sharper resonances for water based IR SPR biosensor can be achieved in the 3.5 to 5.5 µm range.

Nano-structured Au films (Au-black) were investigated as IR absorbers and possible solar cell enhancers based on surface plasmon resonance. The characteristic length scales of the structured films vary considerably as a function of deposition parameters, but the absorbance is found to be only weakly correlated with these distributions. Structured Au-black with a broad range of cluster length scales appear to be able to support multiple SPP modes with incident light coupling to the corrugated surface as seen by photoelectron emission microscopy (PEEM) and SPR experiments, supporting the hypothesis that Au-black may be a suitable material for plasmon-resonance enhancement solar-cell efficiency over the broad solar spectrum.
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CHAPTER ONE: INTRODUCTION

Bound electromagnetic waves that propagate along the interface between a dielectric and a conductor exist at frequencies below the plasma frequency of the conductor. Our knowledge and understanding of these “surface plasmon polaritons” (SPPs) has developed slowly over the last century. The first known experimental effects of surface plasmons on metals were observed by Wood in 1902 [1]. Wood observed dark and light bands in the reflection spectrum of a metallic grating. The first theoretical treatment of the so called “Wood’s anomalies” was completed by Rayleigh in 1907 [2]. Rayleigh’s formulation predicted singularities (known as Rayleigh wavelengths) in the electromagnetic scattering from gratings which occurred at wavelengths that coincided with the “Woods anomalies”. The next important break-through wouldn’t occur until 1957 when Ritchie [3] first predicted the excitation of surface plasmons in metallic films by fast electrons. Seemingly unrelated to Ritchie’s prediction, in 1965 Hessel’s theoretical description for “Wood’s anomalies” [4] indicated that two types of anomalies existed. These anomalies, which may or may not coincide, were the singularities predicted by Rayleigh [2] and a resonant type anomaly due to guided waves. Eleven years after his first surface plasmon work, Ritchie [5] showed that the anomalies found in reflection gratings were due to the optical excitation of surface plasmons which would be later classified as the resonant type of “Wood’s anomalies” that Hessel [4] described. In the same year Otto [6] and Kretschmann [7] excited surface plasmons on metal films utilizing a prism as an optical coupler. By this point it was understood that surface plasmons, as we know them now, can be excited optically by means of a grating, prism or by an electron beam. This work focuses on the optical excitation
methods. Currently, the theory of optical excitation of surface plasmons using prisms and of surface plasmon dispersion (presented in chapter 2) is mostly well understood while complicated numerical algorithms are used to describe coupling of surface plasmons via particular grating structures based on rigorous scattering theories.

Figure 1 presents a timeline showing the relevant historical works to this dissertation described in this and the following paragraphs. A more complete history can be found in [8] and [9].

![Timeline of important developments related to this dissertation. Direct surface plasmon developments have lower arrowheads and are indicated in black. Application developments related to this work are shown with colored captions.](image-url)
SPPs are of interest for a variety of optical and optoelectronic applications [8-12]. One application is that of plasmonic waveguides for use in miniaturized optical components. Most of the early work using surface plasmon waveguides used metallic gratings in the visible wavelength regime. The extension of this application to the LWIR would enable the use of silicon based materials which is very advantageous. The field of silicon photonics roughly began in 1986 with the work of Soref and Lorenzo [13] on silicon waveguides in the IR. Up until this point Si was widely used in the semiconductor industry to create miniaturized electrical devices but Soref showed that Si can also be a valuable tool in the rapidly expanding photonics field. A good description of recent advances in the silicon photonics field can be found in [14].

The first biosensor application was developed by Liedberg and Nylander [15,16], based on the surface plasmon resonance (SPR) in reflection found using metal films by Otto [6] and Kretschmann [7]. This biosensor uses the changes in the SPR to analyze biomolecule interactions. The first commercial surface plasmon resonance biosensor was developed by Biacore in 1991 [17]. More information on the SPR biosensor can be found in [18-20].

Work by Toyama in 2002 [21] gave the first known experimental SPR data on films of nano-strucutered gold called gold-black. The optical properties of metal blacks have been investigated since Pfund’s work in 1933 [22]. Metal-black nano-structured conducting films have been exploited as broad-band surface absorbers for bolometers [23-25]. The SPR characteristics of gold-black has potential in the biosensor application as discussed in [21] and to increase the efficiency of thin film solar cells via resonant scattering and field enhancement.

This dissertation work focuses on the extension of the use of surface plasmons into the IR which has numerous advantages for the biosensor and waveguide applications (to be discussed in
the following chapters). IR surface plasmons are investigated based on both grating and prism coupling techniques for various metal, semiconductor and semimetals. The development and characterization of gold-black films is investigated with reference to applications as an IR absorber, solar cell enhancer, and a possible SPR biosensor host.

The subsequent chapters of this dissertation are organized in the following manner:

- Chapter 2: This chapter gives the basic theoretical formulas for surface plasmons excited optically. Applications such as the SPR biosensor and waveguides are discussed. The characterization methods used for surface plasmon host materials throughout this work are given as well as the experimental techniques used in surface plasmon reflectance measurements.

- Chapter 3: The theory of Hessel and Oliner [4] is presented here and analyzed for later use. Experimental SPR reflectance measurements on Ag gratings are used with this theory to effectively determine a simplified analytic formula useful for designing gratings for use in the long-wave IR wavelength regime.

- Chapter 4: General surface plasmon theory is presented for the calculation of surface plasmon resonances on thin metallic films using prism couplers. Experimental results are given for Au-films in the visible and IR. A discussion on advantages and disadvantages of prisms with different configurations for IR use is also presented.

- Chapter 5: IR optical constants of metal silicides and doped-Si are investigated. Experimental measurements of permittivities for these materials are used to calculate surface plasmon properties and the use of these silicon-based materials in plasmonic applications is discussed.
• Chapter 6: Antimony is investigated as a possible IR surface plasmon host. Experimental reflection resonances are presented for antimony in the long-wave IR above the plasma frequency. A discussion on the origin of these resonances and the use of antimony for plasmonic devices is presented.

• Chapter 7: Materials for an IR surface plasmon biosensor are investigated. Calculated and experimental surface plasmon resonances are shown for multiple SPP hosts which includes metals, semimetals, semiconductors and a conducting polymer. The effects of water on the IR SPR biosensor are analyzed.

• Chapter 8: Au-black films are developed and characterized. A possible correlation between the Au-black cluster size and IR absorption is investigated. Effects of a polymer infusion on the Au-black films are investigated in terms of the physical hardness and IR absorption. Surface plasmon resonance effects are observed and discussed.

• Chapter 9: The work that has been completed in this dissertation is summarized and future work is speculated.
CHAPTER TWO: LONG-WAVE IR SURFACE PLASMONS

2.1 Introduction

In the long-wave IR (LWIR), SPP properties are adequately modeled using Drude theory which casts the frequency-dependent permittivity in terms of a bulk plasmon frequency $\omega_p$ and an electron relaxation frequency $\omega_r$. In general, a negative value for the real part of the permittivity is required to sustain an SPP. Knowledge of material permittivity, or equivalently the bulk plasmon and relaxation frequencies, is essential when considering new materials for LWIR applications. The traditional SPP hosts are noble metals for use in the visible, but semimetals and doped semiconductors have been considered [26-31] at longer wavelengths. The use of non-traditional Si-based SPP hosts warrant consideration because of their inherent CMOS compatibility, which could benefit Si photonics and enable surface plasmon resonance (SPR) biosensors operating at vibrational-fingerprint wavelengths [32-25]. All semimetals and doped semiconductors investigated here are potentially useful in waveguide applications and the previously mentioned SPR biosensor.

2.2 General Surface Plasmon Theory

Surface plasmon polaritons bound at a dielectric / conductor interface have electric field lines that oscillate according to Figure 2 in the $x$-direction along the interface and decay in the $z$-direction above and below the interface as pictured. The usual complex surface plasmon wavevector is found by
\[ k_{spp}(\omega) = \frac{\omega}{c} \sqrt{\varepsilon_d \varepsilon_c \over \varepsilon_d + \varepsilon_c}, \]  

(2.1)

where \( \varepsilon_d \) and \( \varepsilon_c \) are the complex permittivities of the dielectric and conductor respectively. \( k_{spp} \) is in the direction of plasmon propagation (x direction). The complex wavevector of the plasmon in the z-direction is

\[ k_{zd, ze} = \sqrt{\varepsilon_{d,c} \left( \frac{\omega}{c} \right)^2 - k_{spp}^2}. \]  

(2.2)

where \( k_{zd} \) refers to the dielectric region with \( z > 0 \) and \( k_{ze} \) refers to the conducting region with \( z < 0 \). Plasmons bound to a dielectric / conductor interface have an electric field that decays exponentially in the x and z-direction. The magnitude of the surface plasmon electric field is given as

\[ E_{sp} = C(\omega) \Re\left\{ \exp\left[i \left( k_{spp} x - k_z z - \omega t \right) \right] \right\}, \]  

(2.3)

where \( k_z \) is found from Eq. 2.2 for the correct region (dielectric or conductor) and \( C \) is some constant for a given frequency. The positive and negative signs in the x and z terms give the expected exponential decay in all directions.
In Drude theory, the real $\varepsilon'$ and imaginary $\varepsilon''$ parts of the complex permittivity are [36]

$$
\varepsilon' = \varepsilon_\infty \left[ 1 - \frac{\omega_p^2}{\omega^2 \left( 1 + \omega^2 / \omega_\tau^2 \right)} \right],
$$

(2.4)

and

$$
\varepsilon'' = \frac{\varepsilon_\infty \omega_p^2}{\omega_\tau \omega \left( 1 + \omega^2 / \omega_\tau^2 \right)},
$$

(2.5)

where $\varepsilon_\infty$ is the permittivity of the material at frequencies well above the bulk plasmon frequency $\omega_p$. The relaxation frequency is $\omega_\tau = 1/\tau$ where $\tau$ is the relaxation time. For metals, $\varepsilon_\infty$ is generally taken as unity since it is assumed that the charge carrier concentration is sufficiently high to screen the polarization of the lattice. In the infrared, the real part of the permittivity is generally negative and much larger than the imaginary for noble metals which can be implemented by assuming $\omega_\tau = 0$. With this assumption, the permittivity of the conductor is
represented simply by $\varepsilon_c = \varepsilon_x \left(1 - \omega_p^2/\omega^2\right)$ and when substituted into Eq. 2.1 the limits for the dispersion relation can be derived. Figure 3 shows the surface plasmon dispersion relation based on Eqs. 2.1 and 2.4-2.5. At low frequencies for bound SPP’s, the dispersion curve follows the light line. For optical frequencies approaching the limit $\omega < \omega_p \sqrt{\varepsilon_x / (\varepsilon_x + \varepsilon_d)}$, $k_{spp}$ approaches infinity. Between this frequency and $\omega_p$ lies a forbidden gap region where surface plasmons cannot exist. Above $\omega_p$ is the region of unbound (or radiative) SPP’s. It is important to note that for metals with $\varepsilon_x = 1$, the well known limit for bound surface plasmon modes of $\omega < \omega_p / \sqrt{1 + \varepsilon_d}$ is recovered. Another note is that in the case where $\varepsilon_x >> \varepsilon_d$, the forbidden gap tends to vanish.

![Figure 3: General surface plasmon dispersion curve.](image-url)
For the IR range of interest with semimetals or doped semiconductors the assumption of negligible $\omega_\tau$ and $\varepsilon_\infty = 1$ is no longer valid. For noble metals in visible light $\omega_\tau$ can be typically 3 orders of magnitude smaller than $\omega_p$. For many of the materials investigated here in the IR, this is not the case. Figure 4 shows the effects of increasing $\omega_\tau$ to only one order of magnitude smaller than the $\omega_p$ which will be nearly the case for many of the investigated materials in the IR. For some of the investigated semimetals and semiconductors, $\varepsilon_\infty$ can be near 10 or even up to $\sim$ 100. Figure 5 shows the effects of increasing $\varepsilon_\infty$ on the surface plasmon dispersion curve with $\omega_p$ and $\omega_\tau$ near the expected ratios for IR. In the case with $\varepsilon_\infty = 100$, the dispersion curve is nearly the same as the light line with a slight crossing between the bound and unbound SPP region at the plasma frequency.

![Surface plasmon dispersion curve with $\omega_p = 1$, $\varepsilon_\infty = 1$, and increasing $\omega_\tau$. Final $\omega_p/\omega_\tau$ is comparable to what is expected in the IR range with materials investigated here.](image)

Figure 4: Surface plasmon dispersion curve with $\omega_p = 1$, $\varepsilon_\infty = 1$, and increasing $\omega_\tau$. Final $\omega_p/\omega_\tau$ is comparable to what is expected in the IR range with materials investigated here.
Surface plasmons cannot be excited at a dielectric/conductor interface by light with simple illumination. Some coupling mechanism must be used which is usually either a grating or prism with each case giving a method for momentum matching at the interface. For an SPP to exist, the surface plasmon wavevector \( k_{spp} \) must match the incident wavevector on the interface \( k_x \). The usual expression [37,38] for \( k_x \) on a grating is

\[
\text{Re}[k_x] = \frac{\omega}{c} \left[ n_d \sin(\theta) + \frac{m\lambda}{p} \right],
\]  

(2.6)

where \( p \) is the grating period and \( m \) is an integer order of either sign. \( n_d \) is the refractive index of the dielectric above the grating which in most of the cases here is unity with the dielectric region being air but this factor must be included for biosensing applications. SPP’s occur when the right side of Eq. 2.6 equals the right side of Eq. 2.1. For prism coupling \( k_x \) is given by
\[ Re[k_x] = \frac{\omega}{c} n_p \sin(\theta) \quad , \]  

(2.7)

where \( n_p \) is the refractive index of the prism. Similarly, SPP’s occur when Eq. 2.7 matches Eq. 2.1. Our experiment considers only positive angles of incidence \( \theta \).

2.3 SPR Biosensor and Plasmonic Waveguides

Thin dielectric films on a conducting surface strongly affect SPP’s, providing a means for real-time label-free sensing and monitoring of biological entities from molecules to cells. Surface plasmon resonance (SPR) biosensors have become a sensitive label-free method to study biological interactions [39-41] e.g. those marketed by Biacore or Texas Instruments. Established sensors are based on wavelength and angle dependent resonances in attenuated total reflection (ATR) devices using visible/near-infrared light.

The LWIR is proposed for the operational region using semiconductor or semimetal materials because of a number of potential advantages. The LWIR is defined roughly as the 8-12 micron wavelength range, which corresponds to a band of high atmospheric transmission. In comparison with current commercial visible/near-IR systems, enhanced sensitivity and specificity are anticipated due to large index changes that will accompany IR vibrational modes for particular biomolecules. Semiconductor quantum cascade lasers have become available throughout this range. Silicon is highly transparent here, and silicon-based devices offer benefits of integrated manufacturing, miniaturization, micro-fluidic sampling making the use of Silicon-based materials ideal for the attenuated total reflection (ATR) configuration, or prism
configuration. Because the ATR method works in the regime of total internal reflection, silicon allows observation of larger index values for the sample of interest, up to ~3.4, than can be observed in the visible with glass prisms (n ~1.5).

The SPR biosensor will be investigated here by two SPP coupling schemes: the prism (ATR configuration) as discussed and by diffraction gratings. In each configuration, a flow channel would be attached to the conducting film or grating as seen in the schematic in Figure 6 for the prism coupling method and Figure 7 for the grating coupling method. The surface of the conducting film or grating is functionalized with biomolecule recognition elements that reversibly capture specific analyte biomolecules from the flow channel. This results in a refractive index change within a few 100 nm of the surface, which is sensed by the SPP field, causing a shift in the SPP resonance angle.

![Figure 6: SPR Biosensor - Prism coupling.](image-url)
Plasmonic waveguides are another possible application to this work. Silicon plasmonics is an emerging field [30] that can be benefitted by the development of waveguides designed for the LWIR. Si-based SPR waveguides can offer the benefit of integrated manufacturing as with the SPR biosensor. Other semiconductor or semimetal SPP hosts in the LWIR can also be beneficial to waveguide applications.

In this work, conducting films with plasma frequencies in the IR are considered as surface plasmon hosts as opposed to the usual noble metals. The lower carrier concentration and plasma frequency of semimetals and semiconductors relative to metals pushes the surface plasmon dispersion curve farther from the light line in the IR. Surface plasmons on these hosts offer tighter mode confinement to increase the sensitivity to thin dielectric absorbates [30].

Calculation of the decay length and penetration depth of the SPP electric field is important for determining how useful a particular grating is for waveguide and biosensor applications. The energy decay length (1/2 of the electric field decay length) in the direction of propagation, $L_x$, is given by
The 1/e penetration depth of the SPP electric field [38] into the dielectric, $L_d$, or the conductor, $L_c$, are given by

\[
L_{d,c} = \frac{\omega}{c} \text{Re} \left[ \frac{-\varepsilon_{d,c}^2}{\varepsilon_d + \varepsilon_c} \right]^{-1}.
\]  

\[ (2.9) \]

### 2.4 General Characterization Methods for SPP Hosts

Various materials were studied as surface plasmon hosts with either gratings or films being developed. In the case of the latter, conducting films were deposited onto suitable substrates for characterization purposes while some films were deposited onto prisms for surface plasmon experimentation. The methods for developing and specific characterization techniques of surface plasmon hosts will be discussed in their respective sections.

Complex permittivities of optically thick samples were determined using a J.A. Woollam IR-VASE and V-VASE ellipsometers in the IR and visible wavelength regions, respectively. The raw ellipsometer output was used to calculate permittivity data based on standard Fresnel equations assuming an optically thick film [42]. The raw ellipsometer output is $\Psi$, the complex reflectance ratio of p-polarized light to s-polarized, and $\Delta$, the phase shift between the two complex reflectances. From these wavelength dependent measured parameters, the complex permittivity can be determined for a given angle of incidence $\theta$ by

\[ L_s = \frac{1}{2 \text{Im} \left( k_{spp} (\omega) \right)}.
\]  

\[ (2.8) \]
\[ \varepsilon' = \sin^2(\theta) \left[ 1 + \frac{\tan^2(\theta) \left( \cos^2(2\Psi) - \sin^2(\Delta) \sin^2(2\Psi) \right)}{(1 + \sin(2\Psi) \cos(\Delta))^2} \right], \tag{2.10} \]

and

\[ \varepsilon'' = \frac{\sin^2(\theta) \tan^2(\theta) \sin(4\Psi) \sin(\Delta)}{(1 + \sin(2\Psi) \cos(\Delta))^2}. \tag{2.11} \]

The refractive index \( n \) and extinction coefficient \( k \) are then found from the complex permittivity by

\[ \varepsilon = \varepsilon' + i\varepsilon'' = (n - ik)^2, \tag{2.12} \]

as expected. For all ellipsometry measurements, three angles of incidence were used (60°, 65° and 70°), and the respective calculated optical constants (using Eqs. 2.10-2.13) were averaged for each wavelength data point measured.

Infrared transmittance \( T \) and reflectance \( R \) spectra were collected using a BOMEM DA8 Fourier transform spectrometer for various deposited films. Resources were a globar or mercury lamp source, a 4 K Bolometer, HgCdTe or DTGS detector, and Mylar or KBr beamsplitters. Transmittance measurements used a clean DSP silicon substrate as a reference while reflectance measurements used a Au-coated silicon substrate.

Transmission measurements of deposited thin films allow a determination of the skin depth. Knowledge of the skin depth is used to insure that the films subsequently prepared for ellipsometry measurements were optically thick. The optical skin depth of the sample is determined by two methods. Transmittance of a thin film is taken as

\[ T(\lambda) = a \exp \left[ -2d / \delta(\lambda) \right], \tag{2.13} \]
where \( d \) is the film thickness, \( \delta \) the 1/e decay length of electric field into the conductor, \( \lambda \) the wavelength and \( a \) is assumed a constant with some dependence on reflectance. Taking the ratio of transmittance for samples with different metal thickness allows \( \delta \) to be determined according to

\[
\delta = 2(d_2 - d_1)\left[ \ln \left( \frac{T_1(\lambda)}{T_2(\lambda)} \right) \right]^{-1}.
\] (2.14)

The optical skin depth of the sample based on its measured optical constants is found from

\[
\delta = \frac{c}{\omega k},
\] (2.15)

where the extinction coefficient \( (k) \) is directly obtained from empirical permittivity.

The resistivities of some films were measured via four point probe measurements. This can be compared also with resistivity calculated from the Drude parameters according to

\[
\rho = \omega_t \left[ \varepsilon_\infty (\varepsilon' - \omega_p^2) \right].
\] (2.16)

### 2.5 Experimental Techniques for SPR Reflectance Spectra

Surface plasmons cannot be excited with polarized light alone. A coupling mechanism must be used, the three most well known being a prism, corrugated surface (grating) or in some cases electron beam. Experiments completed here will show results for the first two SPP coupling techniques.

Surface plasmon reflection experiments were carried out with gratings or coated prisms by mounting and aligning on a motorized goniometer. Specular reflectance as a function of
incidence angle was measured for the gratings or coated prisms using a quantum cascade laser (QCL) and 77 K HgCdTe detector or using a line-tunable CO\textsubscript{2} laser and power meter. In all cases, the laser radiation was p-polarized, i.e. with the electric field vector in the plane of incidence. The samples and detector were mounted on the $\theta$ and $2\theta$ parts of the motorized goniometer, respectively. SPP generation was observed as a resonant decrease in the reflected intensity at certain angles. In some cases, a boxcar was used increase the signal to noise in real time. Figure 8 shows a schematic and a picture of the experimental setup for measuring specular reflection of a coated prism or conducting grating respectively. The difference between the two coupling schemes (to be discussed in more detail later) is that for the coated prism (Figure 6) the SPP is excited after the light decays through the conducting film while for the grating the SPP is excited at the boundary of incidence.

![Figure 8: Specular reflection setup for surface plasmon measurements. Picture of experimental measurement with grating coupler. The base is a motorized goniometer. The source is a QCL (right side) and the measurement is done by a 77K HgCdTe detector (left side).](image)
3.1 Introduction

Gratings are key in proposed nanophotonic integrated circuits for both the in-coupling of free electromagnetic waves into bound SPP’s and the out-coupling of SPP’s into freely propagating optical fields. Proper grating design is essential in order to achieve efficient couplers that provide good beam-profiles [43]. This chapter considers effects of wavelength and grating amplitude for lamellar gratings (rectangular-groove profiles) on SPP generation. Most SPP studies have been at visible and near IR frequencies, but LWIR is emphasized here.

Photon-SPP coupling for Ag sinusoidal gratings of different amplitudes has been studied experimentally in [44,45] at visible wavelengths. In [44], SPPs were excited by electron beams, and the angular position and angular width of out-coupled light at a given wavelength was recorded. In [45], specular reflection of monochromatic light from gratings revealed dips at certain angles of incidence when light energy was converted to SPPs. Shifts and broadening of the angular resonances with increasing grating amplitudes up to about 10% of \( \lambda \) were reported, but there was no comparison to theory. Hutley [46], observing absorption resonances in diffracted light for nominally sinusoidal gratings of amplitude in the range 0.12 \( \lambda \) to 0.7 \( \lambda \), also reported broadening and shifts. The present LWIR study is of gratings with amplitude in the range 0.01 \( \lambda \) to 0.5 \( \lambda \).
A number of similar experiments, complemented by numerical simulations, reported effects of grating amplitude on angle or wavelength of resonances in reflection from metallic or dielectric gratings of various morphologies [47-51]. The longest wavelength in any of these studies was 5 µm [48]. Goals of this work include the extension of grating couplers to the LWIR, where the permittivity is significantly different than at wavelengths ≤ 5 µm and to demonstrate a simple analytic formula useful for the design and optimization of grating couplers.

The most widely-cited analytic formulation of the grating coupler problem is that of Hessel and Oliner [4]. A review of all 323 citations of [4] indicates that apparently no application of that formulation to experimental results or SPP coupler design has been published. The formulas are, in fact, somewhat complicated, but this work demonstrates certain simplifications that facilitate relatively simple calculations of angular resonance spectra. These simplified calculations agree adequately with experiments on lamellar gratings in the 6-10 µm wavelength range at least for engineering purposes. Though broadening is adequately represented in the calculations, the theory does not predict the small but definite angular shift that occurs with increasing grating amplitude, unless the permittivity is adjusted to account for the increasing surface porosity. These shifts, however, amount to only three-tenths of a degree at the maximum grating amplitude deemed useable for an SPP coupler and thus likely will have little impact on SPP coupler applications.

An essential parameter in the theory is the surface-impedance modulation index, $M$, which is an unspecified function of grating amplitude, wavelength, permittivity and geometry of the grating. Presented here are empirical values for the modulation index determined by fitting theory to experimental data for the wavelengths and grating amplitudes investigated. $M$ is found
to vary linearly with wavelength and as a second order polynomial with grating amplitude, up to values of grating amplitude considered useful for plasmon couplers.

It is possible to obtain a more accurate description of experimental observations using numerical methods [52-55]. However, it may be difficult to obtain intuitive understanding or interpretation of the observed phenomena without running numerous numerical experiments. Moreover, the codes elaborated from rigorous scattering theories are generally part of very expensive commercial software packages, the learning curve for the use of such packages is steep, and the physics behind the code often obscure. Hence, there is value in having, as an alternative, simple approximate analytic formulas that optical engineers may use to design a reasonably effective grating coupler.

3.2 Surface Plasmon Grating Theory

Hessel and Oliner [4] describe two types of resonances, the usual Rayleigh type corresponding to the emergence or exit of a diffraction order at grazing incidence and a type associated with leaky surface waves supported by the grating. The latter are SPPs. They are leaky because they propagate across a modulated surface that leads to out-coupling back into free photons. For metal gratings of rectangular profile in the LWIR, both resonance types coincide to within 0.02% of the incidence angle.

The theory of Hessel and Oliner [4] models the grating as a modulated surface impedance, $Z(x)$, where $x$ is the coordinate in the plane of the grating and perpendicular to the grooves (as with the dielectric conductor boundary in Figure 2). For purposes of obtaining and
testing simple design formulas, only the first Fourier component of that modulation is retained here, as represented by

\[ Z(x) = Z_0 \left( 1 + M \cos \left( \frac{2\pi x}{p} \right) \right), \quad (3.1) \]

even though the actual gratings have rectangular ridges containing many higher harmonics. The full theory of [4] is more general. The effect of neglecting the higher harmonics is to eliminate higher order SPP resonances from the calculated angular reflectance spectra. In Eq. 3.1, \( M \) is the modulation index (some function of grating permittivity, amplitude, and wavelength) and the grating period is \( p \). The limit for zero modulation is given by

\[ Z_0 = \sqrt{\frac{\mu_0}{(\varepsilon' + i\varepsilon'')\varepsilon_0}} = \frac{377\Omega}{\sqrt{|\varepsilon'|}} \quad (3.2) \]

where \( \mu_0, \varepsilon_0, \) and 377 \( \Omega \) are respectively the permeability, permittivity, and impedance of free space, while \( \varepsilon' \) and \( \varepsilon'' \) are the real and imaginary parts of the relative permittivity for the metal. Equation (3.1) suggests that the average permittivity is also \( Z_0 \), but it is noted that bulk permittivity values in \( Z_0 \) may need to be replaced by effective values for a corrugated surface.

For metals in the infrared, we have \( \varepsilon'' \ll |\varepsilon'| \) and \( \varepsilon' < 0 \), giving for the relative surface impedance

\[ \zeta \equiv \frac{Z_0}{377\Omega} \approx \frac{-i}{\sqrt{|\varepsilon'|}} \quad (3.3) \]

If the imaginary part cannot be neglected, and with \( \varepsilon' = -|\varepsilon'| \), we have

\[ \zeta = -i\left( |\varepsilon'|^2 + \varepsilon''^2 \right)^{1/4} \left\{ \cos \left( \frac{\phi}{2} \right) + i\sin \left( \frac{\phi}{2} \right) \right\} \quad (3.4) \]
where $\phi = \tan^{-1}(\varepsilon''/\varepsilon')$. The experimentally determined permittivity values for our silver films are given in Table 1, together with relative surface impedance values from Equations (3.3) and (3.4).

Table 1: Optical parameters of Ag.

<table>
<thead>
<tr>
<th>$\lambda$(µm)</th>
<th>$\varepsilon'$</th>
<th>$\varepsilon''$</th>
<th>$\zeta$ (Eq. 3.3)</th>
<th>$\zeta$ (Eq. 3.4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>6.14</td>
<td>$2707 \pm 270$</td>
<td>$469 \pm 80$</td>
<td>$-0.0192$</td>
</tr>
<tr>
<td></td>
<td>9.250</td>
<td>$5397 \pm 330$</td>
<td>$1463 \pm 120$</td>
<td>$-0.0136$</td>
</tr>
<tr>
<td></td>
<td>10.591</td>
<td>$6774 \pm 450$</td>
<td>$1971 \pm 300$</td>
<td>$-0.0121$</td>
</tr>
</tbody>
</table>

The magnetic field of the incident p-polarized wave is $H \exp[i(k_s x - \kappa_m z)]$ where the in-plane wavevector $k_s$ is related to the incidence angle by $k_s = k \sin(\theta)$ and $k = 2\pi/\lambda$. The field of the scattered wave is

$$H_s(x,z) = \sum_{m=-\infty}^{\infty} I_m \exp \left[ i \left( k_s + \frac{2\pi m}{p} \right) x + i \kappa_m z \right], \quad (3.5)$$

where $I_m$ is the complex amplitude of the $m^{th}$ spectral order (propagating or not) and

$$\kappa_m = \sqrt{k^2 - \left( k_s + \frac{2\pi m}{p} \right)^2}. \quad (3.6)$$

Note that $m$ is an integer taking both positive and negative values. For sufficiently large $m$, $\kappa_m$ is pure imaginary, the $m^{th}$ Fourier component is exponentially damped in the direction normal to the surface, and no diffracted spectral order is present. Otherwise, $\kappa_m$ is purely real giving the
usual propagating spectral orders of the grating. The vanishing of $\kappa_m$, or identically, the condition for the $m$th diffracted beam to occur at $\pm 90^\circ$, is known as the Rayleigh condition [2] and is the cause of one type of the so-called Wood’s anomalies [1]. Here, propagating spectral orders either emerge or disappear. The diffraction equation, $p(\sin \theta_m - \sin \theta) = m\lambda$, ($\theta_m$ and $\theta$ are both positive when on the opposite sides of the normal), gives the Rayleigh condition as $\sin(\pm \pi/2) - \sin(\theta) = m\lambda/p$ which, when satisfied, results in a redistribution of energy among the various orders, including the zeroth (specular) order $I_0$. The second form of the so-called Woods’s anomalies is a resonance phenomenon, which will now be discussed in terms of the work of Hessel and Oliner [4]. For the geometry previously discussed, the reflectivity, $R$, is given by

$$R = \left| \frac{I_0}{H} \right|^2 = \left| \frac{2D_0 - 4/M}{D_0 + A_1 + B_{-1}} - 1 \right|^2,$$  \hspace{1cm} (3.7)

with

$$D_m = \frac{2}{M} \left[ 1 + \frac{\kappa_m}{\zeta k} \right],$$  \hspace{1cm} (3.8)

$$A_1 = -\left\{ D_1 - \left[ D_2 - (D_3 - ...)^{-1} \right]^{-1} \right\}^{-1},$$  \hspace{1cm} (3.9)

and

$$B_{-1} = -\left\{ D_{-1} - \left[ D_{-2} - (D_{-3} - ...)^{-1} \right]^{-1} \right\}^{-1}.$$  \hspace{1cm} (3.10)

Equations (3.9) and (3.10) are continued fractions. If, at a certain angle, $D_1$ or $D_{-1}$ become small, the other $D_m$ remain large, so that the approximation $A_1 \approx -1/D_1$ and $B_{-1} \approx -1/D_{-1}$ can be made in Equations (3.9) and (3.10). This leads to the following approximation for specular reflection
which is valid for the conditions of our experiment. When \( D_i \) reaches a minimum, a dip in specular reflection will occur. The behavior of \( D_i \) is determined by two complex values, namely, the relative surface impedance \( \zeta \) and \( \kappa_i \). We have

\[
Re[D_i] = \frac{2}{M} \left[ 1 + \frac{\zeta' \kappa_i}{|\zeta|^2 k} \right]
\]

and (with \( \zeta'' = -|\zeta'| \) for metals)

\[
Im[D_i] = \frac{2|\zeta''| |\kappa_i|}{M|\zeta|^2 k}.
\]

As the incidence angle \( \theta \) increases from 0, the Rayleigh condition \( \kappa_i = 0 \) is eventually reached where the \( m = 1 \) diffracted order goes off at grazing angle. Before this occurs, \( \kappa_i \) is real, both parts of \( D_1 \) are positive and slowly varying, and no resonance behavior occurs in this angular regime. When the incidence angle passes the Rayleigh condition for \( m = 1 \), \( \kappa_i \) is pure imaginary and can be written as \( \kappa_i = i|\kappa_i| \). Then

\[
Im[D_i] = \frac{2\zeta''|\kappa_i|}{M|\zeta|^2 k},
\]

which is always positive, and

\[
Re[D_i] = \frac{2}{M} \left[ 1 - \frac{|\zeta''| |\kappa_i|}{|\zeta|^2 k} \right].
\]
Equation (3.15) will go to zero, and the specular reflection will reach a minimum, when $|\zeta''| |\kappa_i| = |\zeta|^2 k$. This immediately leads to the condition for resonance-type anomalies in terms of the relative surface impedance as

$$\sin(\theta) + \frac{\lambda}{p} = \sqrt{1 + \frac{|\zeta|^4}{|\zeta''|^2}}. \quad (3.16)$$

A feature of the observed reflection anomalies is their asymmetry. To clarify the origin of asymmetry in the resonance line shapes, Equation (3.7) is rewritten in terms of the real and imaginary parts of each of the complex factors as

$$R = \frac{(D'_0 + A'_1 + B_{-1})^2 + \left(\frac{4 \cos(\theta)}{M|\zeta|} - D''_0 - A''_1 - B_{-1}''\right)^2}{(D'_0 + A'_1 + B_{-1})^2 + (D''_0 + A''_1 + B_{-1}'')^2} \quad (3.17)$$

In Equation (3.17), $\zeta$ is taken to be purely imaginary as in Equation (3.3). The vanishing of $D_1$ causes a derivative-like resonance line shape in $A_1'$ and an asymmetric peak in $A_1''$, while all other factors in Equation (3.17) vary slowly with $\theta$.

When more terms are kept in the continued fractions of Equations (3.9) and (3.10), progressively weaker resonances can be observed whenever $D_m = 0$. The weakening of the resonances with increasing order results from the neglect of higher harmonics in the Fourier expansion of the grating (Equation (3.1)), but including these harmonics results in a much more complicated formula for $R$. Consequently, we limit our calculations to the $m = 1$ resonance, although our experiments reveal also the $m = -3$ resonance. This should still permit adequate SPP coupler design.
According to the discussion above, minima in R (Equation (3.11)) occur when $D_1'$ (Equation (3.15)) becomes small. The vanishing of $D_1'$ with the approximation Equation (3.3) gives the condition for “guided surface wave” generation, namely

$$\sin(\theta) + \frac{\lambda}{p} = \sqrt{\frac{\varepsilon' - 1}{\varepsilon'}}.$$  

(3.18)

This “guided surface wave” must be identified with the SPP of modern literature, since their wavefunctions are the same [4,38], which is given as Eq. 2.6.

The two expressions Equations 3.18 and 2.6, give resonance angles that differ by an insignificant 0.001% for Ag gratings. Figure 9 presents a graphical representation of the SPP resonance condition of Equation 2.6 as it pertains to our experiment. The horizontal axis is the real part of the SPP wavevector, or the component of the incident photon wavevector in the plane of the grating. The vertical axis is the SPP photon energy. The solid lines are SPP dispersion curves, which are close to, but fall below the grazing-incidence light line with slope $hc$. The dashed curves are light lines with slope $hc \sin(\theta)$. All incident angles in our experiment are on the same side of the surface normal and are thus positive, giving positive slopes. The origins of the dashed lines are shifted by integer multiples of the grating momentum $k_g = 2\pi / d$. The shifted light lines intersect the SPP dispersion curves at energies corresponding to the two CO$_2$ laser wavelengths used in this work, as indicated. The angles of incidence necessary for an intersection at the proper CO$_2$ photon energy determine the positions of the resonance absorptions, where SPPs are generated. These angles $\theta$, determined from Equation 2.6 for lines a, b, a’, b’, are 32.5, 22.8, 28.1, and 36.1 degrees, respectively. Note that for the intersections
with lines b and b’, the SPP momentum is negative while the in-plane component of the incident photon is always positive.

Figure 9: Graphical representation of the SPP resonance conditions of this experiment. Solid lines are silver SPP dispersion curves. Light lines (dashed) for different angles of incidence and shifted by different integer multiples of grating momentum are shown. The points of intersection establish the conditions for SPP generation at the wavelengths indicated. Angles of incidence for a, b, a’, b’ are 32.5, 22.8, 28.1, and 36.1° respectively.

3.3 Experimental Considerations for Ag Gratings

Gratings were formed by evaporation of Ag through a photolithographic mask on top of a 200 nm evaporated Ag film supported by a polished silicon substrate. The supporting Ag film is optically thick in the IR. The period of all gratings was 20 μm and the duty cycle was 50%, but the grating amplitude was varied by varying the evaporation time. Measured profiles (KLA Tencor) determine the peak to peak amplitude $h$ of the gratings and confirm that the grating lines have sharp square edges.
To confirm the generation of propagating SPPs at the resonance angle, some samples were prepared with a second grating separated by 1 cm from the first, also indicated schematically in Figure 10. An IR camera, C, was set up to image this second grating, while all rays from the first grating were blocked from reaching the camera by a screen. With the goniometer, it was convenient to observe the $m = 1$ out-coupled beam, which propagates in a direction parallel to the specularly reflected beam at an out-coupling angle of $\theta$. No attempt was made to observe the other expected out-coupled beams.

![Diagram](image.png)

**Figure 10**: Schematic for measurement of out-coupled SPP’s. P-polarized CO$_2$ laser radiation is incident on the right grating, and specular reflection is monitored as a function of angle of incidence using power meter P. A second grating 1 cm to the left out-couples the SPP that has traveled to it, and this event is imaged with an infrared camera C. The screen S prevents any rays from the first grating reaching the camera.
3.4 Results

The experiment represented by the Figure 10 schematic was performed, and out-coupled light was imaged with the IR camera as coming from the second grating when incoming p-polarized light is incident on the first grating at the resonance angle determined by Equation (2.6) for \( m=1 \). This confirms the generation of a propagating SPP. The light out-coupled at the second grating was confirmed to be highly directional. It was not a diffuse scattering and could only be observed when the IR camera was precisely positioned at the expected out-coupling angle. With the goniometer at the \( m = 1 \) in-coupling resonance, it was inconvenient to observe out-coupled beams for \( m \neq 1 \), and these were not looked for. The calculated characteristic propagation length for SPPs on noble metals at the CO\(_2\) laser wavelength is \( \sim 1 \) cm [30], which is the same as the distance between the two gratings. In samples for which the separation was 2 cm, no out-coupled light from the second grating was detected.

For the \( m = -3 \) in-coupling resonance, the generated SPP propagates opposite to the direction of the in-plane component of the incident wavevector (Figure 9). It was experimentally inconvenient to observe out-coupled radiation at a second grating placed to the right of the first (according to Figure 8). Consequently, generation and propagation of an \( m = -3 \) SPP was not directly confirmed by observations. This higher order SPP generation was inferred from the observed dip in reflection from the first grating.

Figure 11 (inset) presents a measured Ag-grating profile before (thin line) and after (thick line) it was annealed for 30 seconds at 850°C. Before annealing, the profile is rectangular. After annealing, the profile has become more sinusoidal except for small bumps on the edges of each
Figure 11 presents the Fourier transform of the grating profiles in the inset (including additional periods), with labeled peaks corresponding to the multiples of the fundamental spatial frequency. The as-deposited profile (thin line) has clear Fourier components up to 6 times the fundamental. The annealed profile (thick line) has mainly the fundamental, with a small contribution at 5 times the fundamental to account for the bumps on the edges. Notable for the experiments reported here is that the peak corresponding to 3 times the fundamental is strongly attenuated by annealing. As will be shown, the effect is to strongly reduce the SPP coupling for $m = -3$. Note that the strength of the fundamental is also reduced by annealing, which has the effect of reducing the $m = 1$ SPP coupling.

![Fourier transform of a measured profile (inset) for as-deposited (thin line) and annealed (thick line) Ag gratings with amplitude of 1 μm.](image)
Figure 12 presents the reflected intensity as a function of angle of incidence for the Ag grating with 1 μm amplitude, before (thin line) and after (thick line) annealing, for two different CO₂ laser wavelengths. Two resonances are observed at each wavelength corresponding to different amounts of grating momentum added to allow generation of a surface plasmon. A third resonance predicted near normal incidence is inaccessible to the experiment. Calculated resonance angles $\theta$ from Equation (2.6) with permittivity values from Table 1 are indicated by symbols. The observed resonances are labeled by the corresponding $m$ value from Equation (2.6). These resonances are approximately symmetrical about the Littrow angle $\sin \theta_L = -m\lambda / 2p$ for $m = -2$, similarly to [46]. The $m = -3$ resonance corresponds to an SPP momentum that is opposite the in-plane component of the incident photon momentum (Figure 9).
The non-repeatable sloping baselines in Figure 12, due to laser power drift, can be ignored. Otherwise, the baseline at the Littrow angle is higher (lower) for \( \lambda/p \) greater than (less than) the value \( \frac{1}{2} \), as was noted in [46]. If \( \lambda/p = \frac{1}{2} \), we would have the \( m = +3 \), and -1 diffraction orders passing simultaneously off the grating horizon for \( \theta = 30^\circ \). We have chosen \( \lambda/p \) values on either side of the value \( \frac{1}{2} \). As \( \theta \) sweeps through the range of observation for \( \lambda/p > \frac{1}{2} \), the number of allowed diffracted orders (not including spectral reflection), changes from 3 to 2 and back to 3. This explains why the power in the specular beam is higher in the central region where the total out-coupled power is shared only among two spectral orders as opposed to three. When \( \lambda/p < \frac{1}{2} \), the number of diffracted orders follow the sequences 3→4→3 so that the opposite situation holds for the specular intensity when compared to the previous case.

From Figure 12 it is clear that, first, the \( m = -3 \) resonance nearly disappears for the annealed sample. Second, the \( m = 1 \) resonance is reduced in amplitude. Third, the resonance angle undergoes a small shift, with the positions for the annealed sample being closer to the calculated positions. Fourth, the \( m = -3 \) resonance angle exceeds the \( m = 1 \) resonance angle at the 10.591 \( \mu \)m excitation wavelength while the opposite is true for the 9.250 \( \mu \)m excitation wavelength.

Figure 13 presents the experimental reflected intensity at the two different CO\(_2\) laser wavelengths for gratings of different amplitude \( h \). For \( h = 100 \) nm, absorption resonances were observed to be at the same level as the background noise. Discernable resonances first appear weakly at \( h = 200 \) nm, where the \( n = 1 \) resonances occur at 32.58 and 28.14° for \( \lambda = 9.250 \) and 10.591 \( \mu \)m, respectively. These values are in good agreement with those calculated from
Equation (2.6) of 32.52° and 28.07° with the discrepancy possibly due to systematic error from the estimate of the origin of the angle scale. The resonances are deepest at $h = 1$ μm, but by 2 μm they are strongly deformed and broadened. As in Figure 12, the $m = 1$ and $m = -3$ resonances switch places when the wavelength is changed from one extreme value of the CO$_2$ laser range to the other. The $m = 1$ resonance is always sharpest on the side of low angles, and the baseline of the reflection is lower on that side. For $m = -3$, the opposite holds.

Figure 13: Measured angular reflectance for two different p-polarized CO$_2$ laser wavelengths and Ag gratings with different amplitudes.

Figure 14 presents calculated resonance spectra according to Equation (3.11). Since a sinusoidal surface impedance variation is assumed with no higher harmonics (Equation (3.1)),
we see only the $m = 1$ resonance, as in Figure 12 for the annealed grating. The observed resonance peaks for the smallest $h$ value are 32.52 and 28.07°, in exact agreement with the values calculated from Equation (2.6). In this figure the surface impedance modulation amplitude $M$ was the only fitting parameter, and its value was adjusted until the calculated curves had the best qualitative agreement with the observed ones. For $h \leq 1 \mu\text{m}$, the depth of the resonance was the main factor in judging the goodness of the fit. For $h > 1 \mu\text{m}$, the lines are distorted, so that other considerations, such as the amplitude of the baseline on either side of the resonance came into play. Notable differences between theory and experiment are in the upward spikes, and the absence of any shift in the theoretical resonance positions with increasing $h$. For grating depths up to ~10% of the LWIR wavelengths, the angle at which the reflectance minimum occurs is described by the surface plasmon resonance condition to within a few tenths of a degree.
The Hessel and Oliner [4] theory predicts very sharp features with widths less than 0.05 degrees that we do not observe experimentally. Thus, for our calculation, we have chosen a step size of 0.05°, which seems reasonable as a bound on the angular resolution of our experiments. The sharpest features observed have widths of about 0.2°. The sharp calculated features broaden at grating amplitudes \( \geq 2 \mu m \) such that an angular resolution of 0.5° was required to eliminate them. This suggests that these sharp structures may be theoretical artifacts.

Figure 15 (inset) compares in detail the calculated and observed resonances for \( h = 0.5 \mu m \) and \( \lambda = 10.591 \mu m \). Line shape and depth were the primary considerations in judging the fit. Because the theory fails to account for the shift with that occurs with increasing \( h \), the
calculation is shifted horizontally by $\sim0.1^\circ$ to match the data. Because the experiment does not give absolute reflectance, the calculation is also shifted vertically.

Figure 15 presents the fit values of the surface impedance modulation parameter $M$ as a function of the grating amplitude. Uncertainty in $M$ values is smaller than the symbol size except for the 1 $\mu$m gratings, where the uncertainty is $\sim10\%$. $M$ values for the 6.14 $\mu$m wavelength are also included. For $h > 1$ $\mu$m, the distortion of the observed resonances and increasing disagreement between calculated and observed line-shapes leads to larger uncertainty, so these data are left out of the Figure 15 fits. Two effects are clear in Figure 15. The surface impedance modulation depends non-linearly on grating amplitude, and it depends on the IR wavelength. The curves in Figure 15 are fits of the function

$$M(h, \lambda) = \alpha(\lambda)h + \beta(\lambda)h^2.$$  \hspace{1cm} (3.19)

Fit values of $\alpha$ and $\beta$ are given in Table 2.

---

**Table 2:** Fitting parameters for $M$ vs $h$, according to Equation (3.19). The largest grating amplitude data point used in the linear fits was 1 $\mu$m.

<table>
<thead>
<tr>
<th>$\lambda$ ($\mu$m)</th>
<th>$\alpha$ ($\lambda$) ($\mu$m$^{-1}$)</th>
<th>$\beta$ ($\lambda$) ($\mu$m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.14</td>
<td>2.76</td>
<td>17.2</td>
</tr>
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<td>9.250</td>
<td>13.6</td>
<td>4.38</td>
</tr>
<tr>
<td>10.591</td>
<td>19.3</td>
<td>-4.26</td>
</tr>
</tbody>
</table>

---

37
Figure 15: Surface impedance modulation parameter $M$ (symbols) determined from fit of theory to observed resonances for grating amplitudes up to $1 \mu m$. Solid lines are quadratic fits. (inset) Measured (thick line) angular reflectance spectra for Ag grating of $0.5 \mu m$ amplitude at $10.591 \mu m$ wavelength compared with a best fit calculated spectrum (thin line).
Figure 16: Coefficients $\alpha$ and $\beta$ plotted as a function of wavelength (symbols). Linear fitting of these values of the form of Equation (3.20) are plotted (solid lines).

Figure 16 shows that the coefficients $\alpha$ and $\beta$ nearly linear functions of $\lambda$. Lines in Figure 16 are fits to the functions

$$
\alpha(\lambda) = a_0 + a_1 \lambda
$$

$$
\beta(\lambda) = b_0 + b_1 \lambda
$$

(3.20)

where $a_0$, $a_1$, $b_0$, and $b_1$ have values - 20.0 $\mu$m$^{-1}$, 3.69 $\mu$m$^{-2}$, 46.6 $\mu$m$^{-2}$, and - 4.71 $\mu$m$^{-3}$ respectively.
Substituting Equation (3.19) into Equation (3.20) gives a function for the modulation parameter,

\[ M(h, \lambda) = (a_0 + a_1 \lambda) h + (b_0 + b_1 \lambda) h^2 \]  

(3.21)

Thus, an empirical formula for the surface impedance modulation parameter \( M(h, \lambda) \) has been found for silver lamellar gratings in the mid-long wave IR. Figure 17 presents a contour plot of empirical \( M \) values. At short wavelengths, \( M \) increases more rapidly with \( h \) than at larger wavelengths. This simple form for the modulation index appears useful for grating heights up to \( \sim 15\% \) of the IR wavelength.

Figure 17: Contour plot of \( M \) calculated for Ag gratings as a function of wavelength and grating amplitude.
3.5 Discussion

Measured resonance angles deviate from the calculated ones as the grating amplitude is increased. However, this shift amounts to only a few tenths of a degree at the maximum grating height that still gives a deep well-defined resonance. The shift may therefore be considered a secondary effect in the design and optimization of an SPP coupler, where the primary consideration is photon-to-SPP energy conversion.

The observed shift in Figure 12 toward the calculated angles for the annealed 1 μm grating is likely due to the 30% reduction in its amplitude to a value that should give an angular deviation of only ~ 0.1°. An effect on the angles due to the change in profile from rectangular to sinusoidal need not be invoked. The higher harmonics involved in a rectangular profile lead mainly to higher order SPP resonances.

Though the theory [4] predicts no shift in resonance angle with grating amplitude, in contrast to the clear observations reported here and by others [44,45], and though the shifts are concluded to be of secondary importance, there is at least a semi-empirical way to account for them. The theory depends on the complex permittivity, which may be replaced by an effective permittivity for structured metals. For $m = 1$, we take the positive sign in Equation (2.6), and an increase in $k_{spp}$ causes an increase in the resonance angle $\theta$, as observed for the $m = 1$ resonances in Figure 13 when the grating amplitude is increased. If $m = -3$, we take the negative sign in Equation (2.6), and an increase in $k_{spp}$ leads to a decrease in $\theta$ as is observed in Figure 13 for $m = -3$ with increasing $h$. Thus, observed angular shifts can be adequately explained by shifts in the SPP dispersion curve toward higher wavevector values with increasing grating amplitude, as
reported in [44] for e-beam excited SPPs at visible frequencies on sinusoidal Ag gratings.

According to Equation (2.6), if $\varepsilon$ is reduced, then $k_{spp}$ moves to larger values further from the light line ($k = c / \omega$). Thus, the observed shift in resonance angles can be explained by a reduction in the permittivity as the surface becomes more and more structured and porous. A reduction in effective permittivity for a structured metal makes intuitive sense and has precedent [56], though it is possible to explain the shifts without such by numerical methods [52-55].

There appears to be no clear theoretical relationship between the surface impedance modulation parameter $M$ and the experimental parameters $h$ and $\lambda$. Neviere and Vincent [57] give a relation for the grating surface impedance that is proportional to $\left(\frac{h}{\lambda}\right)\cos^2(\theta)$ if $h << \frac{\lambda}{\pi}$. This fails to account for the observed curvature (Figure 15). Moreover, the linear dependence on wavelength that is found is not in agreement with a $\lambda^{-1}$ dependence.

Wirgin and Maradudin [58] give a surface impedance function $Z$ that depends on $\lambda$, $h$, $p$, grating duty, and $\theta$. However, their modulation parameter $M$ is not a function of $h$ but instead the grating duty cycle and $p$. Depine and Brudney [59] give a simple relation $M = \frac{h}{p}$ for the modulation parameter in the Hessel and Oliner [4] surface impedance model. This lacks curvature with $h$, and it has no $\lambda$ dependence, in contrast to what is expected [4] or observed.

References [4,57,58] indicate that SPP resonances are observable in reflection gratings only when the grating amplitude $h < \frac{\lambda}{\left[ 4 \cos(\theta) \right]}$. For our CO$_2$ laser wavelengths (9.250, 10.591 $\mu$m) and the angle of resonance for first order, the limiting amplitude is about 3 $\mu$m, which is in reasonable agreement with the value $h = 2$ $\mu$m where the observed resonances become strongly deformed.
At the LWIR wavelengths studied, it is found both experimentally and theoretically, that the optimum grating amplitude that gave the deepest well-defined resonance was about 10-15% of the wavelength. The resonances were much weaker at 5% grating amplitude. This contrasts with [52], which reported that in the visible on sinusoidal gold gratings the optimum $h/\lambda$ was in the range of 3-6% and decreased as the wavelength increased. It is doubted that there is a fundamental difference in the behavior of sinusoidal and lamellar gratings, as each of the Fourier components for the latter appears to be acting independently and the resonances due to each are well separated in the spectrum. Rather, it appears that in transitioning an SPP coupler to the LWIR, it is insufficient to merely scale all grating dimensions according to wavelength.

An approximate analytic formula for use in the design of SPP grating couplers is presented here. This approach relies on an impedance modulation parameter, which has been determined empirically by fitting the measured the coupling of photons to SPPs for silver lamellar gratings at 6-11 μm wavelengths. The dependence of the surface impedance modulation amplitude on wavelength and grating amplitude agrees poorly with the published expressions. Therefore, without an accurate theory for the dependence of the impedance modulation parameter on wavelength, material, and grating amplitude, a phenomenological dependence must be established so that the approach may be applied widely to the optimization of grating couplers.
CHAPTER FOUR: PRISMS AS IR SURFACE PLASMON COUPLERS

4.1 Introduction

For investigating prisms as an SPP coupling mechanism, traditional gold is used as the conducting SPP host on Ge or Si prisms. Then resonances are sharp, which facilitates the investigation of the coupler. The coupling scheme now considered is the hemicylindrical prism. This choice is based on current art in the visible/near-IR spectral range. The value of this type of prism is that there is no limitation to the range for the angle of incidence, and the angle of incidence is unchanged by refraction, simplifying the analysis. Also with the prism coupler, only a single resonance due to SPP’s occurs as opposed to the multiple resonances that can occur for gratings. With only one resonance, analyzing the reflectance spectra is greatly simplified.

4.2 Surface Plasmon Prism Theory

Calculation methods for prism coupling of SPP’s is much more straightforward than for that of gratings with theory being shown in [60] and [61]. Calculations shown here will treat the incident medium as the prism and the substrate medium as either air or some higher index dielectric material. The incident light is assumed normal to the prism / air boundary so the incident angle at the prism / conductor interface is the same as that experimentally measured outside the prism. In most cases in this work, only the conducting film will lie between the prism and substrate medium. A second film is taken into account in the calculation method since later calculations will include a layer of permittivity corresponding to biomolecules.
For a given angle of incidence $\theta$, the incident wavevector $k_x$ is calculated by Eq. 2.7.

Corresponding $k_{zi}$ components are calculated for each part of the media: the incident prism which is given the subscript $p$, the first film is subscript 1, the second film is subscript 2, and the substrate medium which is given the subscript 3. $k_{zi}$ is calculated by

$$k_{zi} = \sqrt{\varepsilon_i \left(\frac{\omega}{c}\right)^2 - k_x^2}, \quad (4.1)$$

where $\varepsilon_i$ is the permittivity for each region. A complex reflection coefficient $r_{j,j+1}$ is calculated for each boundary by

$$r_{j,j+1} = \frac{k_{zi}/\varepsilon_j - k_{zi(j+1)}/\varepsilon_{j+1}}{k_{zi}/\varepsilon_j + k_{zi(j+1)}/\varepsilon_{j+1}}. \quad (4.2)$$

From Eq. 4.2, a reflection coefficient from the last two boundaries is found by

$$r_{1,3} = \frac{r_{1,2} + r_{2,3} \exp\left(2ik_{zi}d_2\right)}{1 + r_{1,2}r_{2,3} \exp\left(2ik_{zi}d_2\right)}, \quad (4.3)$$

where $d$ is the thickness of the respective film. The final reflection coefficient is found by

$$r_{0,3} = \frac{r_{0,1} + r_{1,3} \exp\left(2ik_{zi}d_1\right)}{1 + r_{0,1}r_{1,3} \exp\left(2ik_{zi}d_1\right)}. \quad (4.4)$$

The final reflectance $R$ is then found by

$$R = \left|r_{0,3}\right|^2. \quad (4.5)$$

For the simplified case of only 1 film (SPP’s on just the conducting film with no biomolecules) the same steps are followed but taking the absolute value squared of Eq. 4.3 instead of Eq. 4.4 with the incident prism medium being represented by the subscript 1.
For prism coupling the surface plasmon reflection resonance will always occur at an angle of incidence higher than the total internal reflection (TIR) angle which is given by

$$\sin(\theta_{TIR}) = n_p^{-1},$$  \hspace{1cm} (4.6)

for a bare prism in air.

4.3 Cylindrical Prism Results

Initial surface plasmon reflectance measurements were completed in the visible with a BK7 cylindrical prism coated with a 45 nm layer of Au to test the experimental design. For this experiment a Xe arc lamp was used with a monochrometer to achieve the specified wavelengths and a photomultiplier tube was used as a detector. Figure 18 shows the experimental measurements compared to calculated reflectance spectra. The experiments carried out in the visible region show clear surface plasmon resonances as expected.
Figure 18: Measured (left) and calculated (right) reflectance spectra using a BK7 cylindrical prism with a 45 nm thick layer of Au at visible wavelengths. The optical constants for Au used in the calculation was from [38] while refractive index for BK7 was taken to be 1.52.

For experiments in the IR wavelengths investigated, the prism must be chosen to have low loss. Initial experiments used a CO$_2$ laser (~10 µm wavelength or ~1000 cm$^{-1}$), where Ge has low loss [62]. Hence, the first hemicylindrical prisms were fabricated from Ge. Silicon was also used because it is cheap, readily available, and for its well developed processing techniques. The loss for Si is higher than for Ge, however [62]. Figure 19 presents photographs of in-house prism-fabrication (left), two finished hemi-cylindrical semiconductor prisms (center), and one commercial Si ATR prism (right). The in-house fabrication used a hollow diamond-tipped drill bit which cuts out a cylindrical shape. The outer surface of the cylinder was hand polished using silicon carbide grit. The polished cylinder was split with a diamond saw and the flat surface hand polished. The left prism in Figure 19 (center) is made from germanium and the right one from silicon (resistivity > 200 Ω-cm). All three prisms in Figure 19 have been gold coated on
their flat surfaces by standard deposited processes with 5 nm of Ti first deposited to promote sticking.

Figure 19: (left) Silicon slab with holes cut using diamond drill bit. (center) Ge and Si hemicylindrical prisms with gold coatings, 1 cm diameter. (right) Commercial Si ATR prism (Korth Kristalle GMBH).

The calculated resonance angle for Au on Ge is 14.5°, which is very close to the critical angle for total internal reflection. The experimental set up used a CO₂ laser operating at 9.552 μm wavelength which was chosen due to a minimum in the Si absorbance [30]. The reflectance data are presented in Figure 20 (left). The data are dominated by fast and slow oscillations, and no resonance is detected near 14.5°. The oscillations are explained as follows. The prism can never be perfectly cylindrical nor can it be cut perfectly on a diameter, so that the internal path length changes with the angle of incidence. A high Q cavity is formed inside the high-index prism between the two spherical surfaces, resulting in high-visibility interference fringes. These oscillations obscure the resonance and are the main disadvantage of hemicylindrical prisms for the IR biosensor application.
Figure 20: Measured reflectance (left) vs. angle of incidence for Ge hemicylindrical prism. (right) Resonance absorption due to creation of SPP for Si prism with 10 nm gold film. The red line is the calculated resonance spectra. This data contains more noise than for Ge due to the higher loss and lower throughput in Si. The wavelength for these measurements was 9.55 µm.

The angular reflectance spectrum for the homemade Si prism is presented in Figure 20 (right). The film was formed by depositing 5 nm of Ti, to promote sticking, followed by 5 nm of Au. Here a resonance is observed close to the expected 17°. Where the absorption is strongest, the fringes are weakest, due to the reduction of the cavity Q. The resonance is much broader than as calculated and is shifted to higher angles of incidence. The commercially-prepared ATR prism turns out to be just as bad. The difficulty in obtaining a clean sharp resonance spectrum without interference fringes suggests that semiconductor hemicylindrical prisms are a poor approach in the measurement of LWIR surface plasmon resonances.

The Fabry-Perot fringes observed in the cylindrical prism measurements leads us to consider a triangular prism coupler which has no internal cavity resonances to cause oscillations in the angular reflection spectrum. The disadvantage is that the prism angle for the high index IR material must be large [33] in order to access the desired angles of incidence at the sensor
surface. Prisms with such angles are not items of commerce and will have to be specially manufactured. Early design work [33] for SPR measurements in the LWIR with semiconducting isosceles prisms indicates that a very obtuse triangular shape is needed with an angle in the range of 115 – 145°. Moreover, the relation between the angles within and outside the prism is non-linear which complicates the analysis.
CHAPTER FIVE: IR PERMITTIVITIES FOR METAL SILICIDES AND DOPED SILICON

5.1 Introduction

In the long-wave IR (LWIR), SPP properties are adequately modeled using Drude theory which casts the frequency-dependent permittivity in terms of a bulk plasmon frequency $\omega_p$ and an electron relaxation frequency $\omega_e$. A negative value for the real part of the permittivity is in general required to sustain an SPP. Knowledge of material permittivity, or equivalently the bulk plasmon and relaxation frequencies, is essential when considering new materials for LWIR applications. The traditional SPP hosts are noble metals, but other materials, such as silicides and doped semiconductors have been considered [28-30] at longer wavelengths. These non-traditional SPP hosts warrant consideration because of their inherent CMOS compatibility, which could benefit Si photonics and enable Surface Plasmon Resonance (SPR) biosensors operating at vibrational-fingerprint wavelengths [34,35].

Optical constants of silicide films prepared by usual industrial processes have been previously investigated using ellipsometry in the visible (NiSi [63], NiSi$_2$ [63], Pd$_2$Si [64], PtSi [65,66], TiSi$_2$ [67]) and into the near-IR (NiSi$_2$ [68]). Reflectance measurements of thin films in conjunction with Kramers-Kronig analysis for NiSi$_2$ [69], PtSi [70] and TiSi$_2$ [71] have determined optical constants out to 124, 31 and 25$\mu$m wavelength, respectively. Transmission and reflection have determined the optical constants of PtSi [72] out to 6$\mu$m. Constants for
single crystals of Pd$_2$S [73] and TiSi$_2$ [74,75] have been determined by reflectance experiments and Kramers-Kronig analysis out to 25, 124, and 21μm, respectively.

This chapter presents experimental determination of the permittivity values for Pt-, Pd-, Ni-, and Ti-silicides as well as n- and p-type doped silicon in the range 1-40 μm. Plasmon and relaxation frequencies are extracted from fits to the Drude model, which allows extrapolation of the permittivity to 100 μm. All results are industrially relevant since the materials were produced by standard processes used in the semiconductor device industry (CMOS processes). Benefits of using metal silicides or doped Si (as opposed to noble metals) in long-wave infrared SPP waveguides are considered in terms of mode confinement and propagation loss.

5.2. Experimental

The silicide samples were prepared by first forming a native oxide on a <100> Si wafer via 10 minute insertion into a UV-Ozone environment. This oxide was subsequently stripped with a hydrofluoric acid dip, rinsed in de-ionized water and blown dry with nitrogen. Electron beam evaporation was used to deposit a Si film, followed by e-beam evaporation of Pt, Pd, Ni or Ti with the film thicknesses given in Table 3. An 800°C, two hour, post metallization anneal diffused the metal into the Si to form the desired silicide. An optically thick Ag layer was deposited on a Si wafer in the same manner as the silicide films for comparison.

Doped Si samples were commercially obtained and had vendor specified resistivities of 0.0018-0.0032 Ω-cm (p-Si) and 0.0006-0.001Ω-cm (p-Si) and <0.014Ω-cm (n-Si). Using the resistivity data for heavily doped p- and n-Si and [76], hole concentrations in the p-Si samples
was determined to be \( 3 \times 10^{19} \text{ cm}^{-3} \) and \( 10^{20} \text{ cm}^{-3} \) respectively, while the electron concentration in the n-Si exceeded \( 2 \times 10^{18} \text{ cm}^{-3} \).

Development of heavily-doped Si on one surface of double-side polished (DSP) undoped silicon wafers was completed by two methods. Implantation of phosphorus (n-type) was performed by Leonard Kroko, Inc. The software TRIM (the Transport of Ions in Matter) was used to determine the correct ion implant schedule. The ion implant schedule was a dose (ions/cm\(^2\)) of \( 9.5 \times 10^{15} \) at 60 keV followed by a \( 2.5 \times 10^{15} \) dose at 30 keV. A 15 minute 900° C post-implant anneal was performed. Diffusion was performed on another undoped DSP Si wafer at the University of Central Florida via continuous source deposition (Phosphorus) for 40 minutes at 950° C. Both ion implantation and diffusion were designed to give carrier concentration profiles in the range of \( 10^{20} \text{ to } 10^{21} \text{ cm}^{-3} \) with thicknesses > 100nm.

Silicide film thicknesses were determined using a standard step profilometer and a PHI Adept Dynamic SIMS (Secondary Ion Mass Spectroscopy) system. A General IONIX 1.7 MU Tandetron RBS (Rutherford Backscattering Spectroscopy) system, with RUMP (Rutherford universal manipulation program) was used to investigate sample stoichiometry [77] as well as silicide film thickness. Four point probe measurements determined sample resistivity. Complex permittivities were determined using by ellipsometry. Finally, film morphology was studied using a Tescan Vega SEM (Scanning Electron Microscopy) and a Phillips XRG 3100 X-ray generator.
5.3. Results

Scanning electron microscopy on the metal silicide films characterizes the film morphology (see Appendix A). The Nickel silicide SEM image is a mosaic of dark and light patches of ~ 2 µm scale in roughly equal proportions. Palladium and Platinum silicide images appear to contain microcrystals with characteristic length scales of 2 and 1 µm respectively. The Titanium silicide film appears uniform and near-featureless, suggesting microcrystals of dimensions significantly smaller than 1 µm.

X-ray diffraction (XRD) experiments were performed and results (see Appendix B) compared to powder diffraction standards (International Center for Diffraction Data, ICDD). All samples were measured using the CuKα₁ and CuKα₂ lines at wavelengths of 1.5406 Å and 1.5444 Å respectively, over an angular range of 20 to 80 degrees with an angular resolution of 0.025 degrees. All samples showed an intense peak identified as the (004) crystal plane of the bulk silicon substrate, as well as a weak (002) peak. The Platinum based film was well indexed (16 peaks) with polycrystalline Platinum Silicon (12.5 wt. % Si), but with a d-spacing 1-2% smaller according to the standard ICDD 7-251. The Palladium based film exhibited only the (400) and (800) planes of Palladium Silicide, indicating strong preferred orientation, and also a 3-6% smaller lattice spacing than the standard for Pd₃Si (ICDD 19-893). The Titanium film was consistent with polycrystalline Titanium Silicide, with a lattice spacing matching the standard for TiSi₂ (ICDD 35-785). The Nickel film was found to be consistent with the (211) and (013) crystal planes of Nickel Silicide, NiSi, (ICDD 38-844) although this film also shows a broad unidentified x-ray peak with a lattice spacing of 1.59 Å of unknown origin.
Thickness values of the silicide layers are summarized in Table 3. The FWHM of the metallic concentration versus depth from SIMS was taken as one measure of film thickness with ~10 nm uncertainty. The profilometer values agree within 10% except for Titanium silicide. The thicknesses from RBS are systematically higher by more than the expected 5% uncertainty. The discrepancy may be due to surface oxide layers.

Table 3: Metal and Si thicknesses used to obtain silicides of this work, silicide characterization results and extracted Drude theory parameters.

<table>
<thead>
<tr>
<th>Si / metal (nm)</th>
<th>Ni</th>
<th>Pd</th>
<th>Pt</th>
<th>Ti</th>
<th>n-Si</th>
<th>p-Si (1)</th>
<th>p-Si (2)</th>
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<td>85/120</td>
<td>132/120</td>
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<td>Profilometer Thickness (nm)</td>
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<td>160</td>
<td>200</td>
<td>180</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SIMS Film Thickness (nm)</td>
<td>240</td>
<td>160</td>
<td>220</td>
<td>230</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RBS Film Thickness (nm)</td>
<td>260</td>
<td>220</td>
<td>260</td>
<td>295</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RBS Composition</td>
<td>NiSi1.38</td>
<td>Pd2.13Si</td>
<td>PtSi1.13</td>
<td>TiSi2.03</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ω_ρ (eV)</td>
<td>3.84</td>
<td>3.63</td>
<td>3.69</td>
<td>3.20</td>
<td>0.036</td>
<td>0.140</td>
<td>0.21</td>
</tr>
<tr>
<td>ω_τ (eV)</td>
<td>0.075</td>
<td>0.049</td>
<td>0.080</td>
<td>0.030</td>
<td>0.037</td>
<td>0.070</td>
<td>0.070</td>
</tr>
<tr>
<td>ρ_{fit} (μΩ-cm)</td>
<td>37.8</td>
<td>27.7</td>
<td>43.7</td>
<td>21.8</td>
<td>18k</td>
<td>2.4k</td>
<td>1k</td>
</tr>
<tr>
<td>Four Point Probe ρ (μΩ-cm)</td>
<td>31</td>
<td>21</td>
<td>31</td>
<td>12</td>
<td>14k</td>
<td>1.8k</td>
<td>-</td>
</tr>
<tr>
<td>Carrier Concentration (cm^{-3})</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2x10^{18}</td>
<td>6x10^{19}</td>
<td>10^{20}</td>
</tr>
</tbody>
</table>

RBS results gave the metal-to-silicon ratios presented in Table 3. For Pd-, Pt-, and Ti-silicides, the ratios are nearly whole numbers. When taking into account the 5% uncertainty, the
stochiometry of these silicides are nearest to Pd$_2$Si, PtSi, and TiSi$_2$. The nickel to silicon ratio deviated significantly from an integer.

Figure 21 presents - $\varepsilon'$ and $\varepsilon''$ spectra for Ag. Infra-red data measured for Ag was conjoined with visible data from [78]. Published $\omega_p$ and $\omega_\tau$ values where used (9.02 and 0.018 eV respectively [79]) to calculate Drude curves, which are plotted for wavelengths beyond 40 $\mu$m.

![Figure 21: Real and imaginary part of permittivity for Ag from ellipsometry data and data from [78]. Dotted lines show Drude fits.](image)

Figure 22 presents permittivity spectra for commercially purchased doped silicon. The $\varepsilon'$ values for the n-Si sample were positive for all wavelengths investigated. Fitting emphasized the $\varepsilon'$ data. Resulting $\omega_p$ and $\omega_\tau$ values are given in Table 3. Extrapolation to wavelengths beyond 40 $\mu$m is plotted in Figure 22.
Secondary ion mass spectroscopy (SIMS) for the ion implanted Si sample shows that the ion concentration follows the calculated (TRIM) curve very closely as seen in Figure 23 (left). The ion concentration reaches a peak of $10^{21}$ cm$^{-3}$ to a depth of at least 100 nm. The actual carrier concentration is lower since not all implanted ions will be electrically activated even after annealing. SIMS analysis of the diffused sample indicates a maximum dopant concentration near the surface of about $2 \times 10^{20}$ cm$^{-3}$ (Figure 23 (middle)). For comparison SIMS was also completed on the n-type commercially purchased Si with ion concentration of $2 \times 10^{18}$ cm$^{-3}$ which is shown in Figure 23 (right).
Complex permittivity was measured for ion-implanted and diffusion Si samples by IR ellipsometry and is presented in Figure 24. Only the diffused sample has a negative $\varepsilon'$ in any part of the IR wavelength space (goes slightly negative around 10.6 $\mu$m wavelength). This suggests that though the implanted sample has the higher ion concentration, it actually has the lower carrier concentration. Since in general a negative $\varepsilon'$ is required to sustain an bound SPP, these data indicate that neither sample has sufficient carrier concentration to support SPPs in the wavelength range of the CO$_2$ laser. Moreover, even where $\varepsilon' < 0$, we have $\varepsilon'' > |\varepsilon'|$, so that any resonance should be broad.

Figure 23: SIMS results showing ion concentration of three doped Si samples. (left) is the Ion-implanted Si, (middle) is the diffusion sample and (right) is the commercially purchased n-type Si sample.
Figure 24: Measured complex permittivity of doped silicon samples produced by ion-implantation and diffusion.

Figure 25 presents permittivity spectra for metal silicides. Drude fits are also plotted (with $\omega_p$ and $\omega_\tau$ values presented in Table 3). The dip in $L_x$ for Pd$_2$Si near 8 $\mu$m are due to a Si-O vibrational absorption [80]. The curves for all silicides are similar at low photon energy. The upper limit for SPPs is significantly lower for Pd- than for the other silicides.

The $\omega_p$ and $\omega_\tau$ values resulting from the fits to the IR data were used in Equation (2.16) to calculate resistivity values, which are tabulated as $\rho_{fit}$ and compared with four point probe values $\rho$ in Table 3. The latter are systematically smaller than the $\rho_{fit}$ values, as was also reported in [69] for various nickel silicides. The highest doped Si was beyond the resistivity range for the four point probe.
Figure 25: Real and imaginary part of permittivity for metal silicides from ellipsometry data. Only negative values of real part are plotted in this figure. Dotted lines show Drude fits.

Figure 26 presents the characteristic plasmon propagation length as a function of free-space photon wavelength. Values calculated from permittivity data are plotted as symbols while the solid lines are extrapolations to longer wavelengths based on Drude theory and the extracted $\omega_p$ and $\omega_\tau$ values. Only the range for which $\varepsilon'<0$ is plotted for each material, except for the n-Si which doesn’t go negative with the extracted values. Because results for silicides are so similar, an average value of propagation length was plotted, with the error bars on the symbols representing the variation. For comparison, near-IR propagation lengths based on measured
permittivity are included for Ag [78]. No experimental values are presented for n-Si in Figure 26 since $\varepsilon' > 0$ for all experimental wavelengths, and the plotted curve is Drude extrapolation.

Figure 26: Propagation length as a function of free space wavelength. Symbols are calculated from experimental permittivity and lines are extrapolations based on Drude fits. The average of Pd, Ti, Ni and Pt-silicides is plotted with error bars indicating the spread in their values. Results for Ag, included for comparison purposes, are calculated from experimental data (ours and [78]).

Figure 27 presents SPP field penetration depth into the conductor $L_c$ (lower curves) and into air $L_d$ (upper curves) as functions of free space wavelength, according to Equation (2.9). All symbols and lines in Figure 27 are as in Figure 26. For Ag, the field penetration depth into air everywhere exceeds the free space wavelength. For silicides, the penetration depth into air is less than the wavelength for $\lambda < 2 \mu m$. For the p-Si and n-Si, the penetration depth is less than the wavelength for $\lambda < \sim 20 \mu m$ and 50 $\mu m$, respectively.
Figure 27: Penetration depths versus free space wavelength. Symbols are calculated from experimental permittivity and lines are extrapolations based on Drude fits. The average of Pd, Ti, Ni and Pt-silicides is plotted with error bars indicating the spread in their values. Upper four curves (triangles) show penetration depth into air while the lower four curves (circles) show penetration depth into the conductor. Results for Ag, included for comparison purposes, are calculated from experimental data (ours and [78]).

5.4 Discussion

The RBS data suggest that the Nickel silicide film is a mixture of NiSi and NiSi₂, while XRD indicates NiSi plus some unknown material. This may explain the mottled appearance in the SEM image if the forms exist in unmixed islands. Reference [63] reports the formation of NiSi₂ for annealing above 700°C and the formation of NiSi at 400°C. Our anneal of 800°C gave a nickel silicide that was most likely in the transition process from NiSi to NiSi₂. Our \( \omega_p \) and \( \omega_\tau \)
values of 3.84 and 0.075 eV respectively fall between those reported [69] for NiSi and NiSi$_2$ (see Table 4).

Table 4: Published silicide Drude parameters and measured resistivity values.

<table>
<thead>
<tr>
<th></th>
<th>NiSi</th>
<th>NiSi$_2$</th>
<th>Pd$_2$Si</th>
<th>PtSi</th>
<th>TiSi$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_p$ (eV)</td>
<td>3.8$^a$</td>
<td>4.6-7.4$^{a,c}$</td>
<td>2.8-3.6$^e$</td>
<td>-</td>
<td>4.2$^i$</td>
</tr>
<tr>
<td>$\omega_\tau$ (eV)</td>
<td>0.035$^a$</td>
<td>0.15-0.25$^{a,c}$</td>
<td>0.03$^e$</td>
<td>-</td>
<td>0.015$^i$</td>
</tr>
<tr>
<td>$\rho_{pub}$ ((\mu\Omega\text{-cm}))</td>
<td>12-36$^{a-b}$</td>
<td>34-60$^{a-d}$</td>
<td>13-35$^{d,f,g}$</td>
<td>28-35$^{d,h}$</td>
<td>10-25$^{d,i-k}$</td>
</tr>
</tbody>
</table>

$^a$Ref. [69], $^b$Ref. [63], $^c$Ref. [68], $^d$Ref. [81], $^e$Ref. [73], $^f$Ref. [82], $^g$Ref. [64], $^h$Ref. [66], $^i$Ref. [74], $^j$Ref. [83], $^k$Ref. [84].

Table 4 presents published Drude parameters for the metal silicides. The $\omega_p$ value in Table 3 for Pd$_2$Si agrees most closely with the measured value (3.6 eV) for polarization parallel to the single crystal c-axis [73]. This result is in agreement with the observation from XRD that the Pd- silicide film consists of highly oriented microcrystals. The Pd$_2$Si relaxation frequencies differ by a factor of 1.6. The PtSi $\omega_p$ and $\omega_\tau$ values in Table 1 and 2 are in good agreement. For TiSi$_2$ $\omega_p$ differs by 30\% while $\omega_\tau$ differs by a factor of 2.

Table 3 lists published resistivity values for silicides, $\rho_{pub}$. Our $\rho$ value for the nickel silicide sample falls into the reported range for NiSi but it is below the range for NiSi$_2$. All $\rho$ values for the other silicides fall within the respective $\rho_{pub}$ ranges.

We have previously modeled [31] the impurity concentration dependence of $\omega_p$ and $\omega_\tau$ in heavily doped Si. For both n-Si and p-Si, and it is found that $\omega_p$ increases by a factor of 3.2
when n (or p) increases from $10^{20}$ cm$^{-3}$ to $10^{21}$ cm$^{-3}$, whereas $\omega_t$ remains essentially constant over that range.

Figure 26 and Figure 27 suggest that silicides are more suitable for SPP applications at photon wavelengths in the range 5 to 100 um [30] than are metal films due to better mode confinement while maintaining an acceptable propagation length. Doped Si is best suited for SPP applications at 50 to 200 um wavelengths, i.e. the THz spectral range for carrier concentrations in the range of those purchased ($10^{18}$-$10^{20}$ cm$^{-3}$). The suitable wavelength range for SPP applications with Doped Si approaches that of the silicides with increasing carrier concentration. These SPP hosts may be exploited in LWIR Surface Plasmon Resonance (SPR) biosensors since characteristic vibrations should yield better specificity and tighter mode confinement [34].
CHAPTER SIX: IR SURFACE PLASMONS ON ANTIMONY

6.1 Introduction

The usual condition for sustaining a surface plasmon is that the real part of the permittivity be negative [30,38]. For usual metals, this condition holds for wavelengths in the visible and beyond. However, the mode-confinement advantages of SPPs occur only at the short-wave part of this spectrum for such metals.

This chapter presents a determination of relevant IR SPP properties for Sb, including the frequency-dependent propagation length and penetration depths for the fields into the media on either side of the interface. These values are calculated using optical constants that were measured over the wavelength range 1 to 40 microns. Plasma and carrier relaxation frequencies are determined from the Drude-model fit to these data. The IR penetration in Sb was measured and compared with the calculations based on the optical constants in the wavelength range 5-11 microns. The usual criterion for bound SPPs is that the real part of the permittivity be negative which occurs for Sb at wavelengths beyond 11 microns. However, there is hardly any distinction between the wavefunction for SPPs on Sb on either side of the transition at 11 microns. It is shown that this is due to the real and imaginary parts of the permittivity being comparable in magnitude.

Infrared SPP applications include plasmonic devices [27,30,31] and biosensors [32,34,39,41]. The biosensor application mainly requires the existence of a suitable SPP-photon
coupling resonance that is sensitive to changes in the permittivity at the conductor-dielectric interface. This work reports the observation of such resonances in the angular reflection spectrum from Sb grating couplers. These resonances appear even though our photon frequencies are in the region of nominally unbound SPPs. The observed resonances compare favorably to calculated spectra. These resonances are potentially useful for IR sensor applications, and their sensitivity to changes in permittivity in the half space above the Sb surface was determined.

6.2 Experimental

Antimony films were thermally evaporated from 99.999% pure Sb pellets. The film thickness was monitored during evaporation using a crystal monitor. Double-side polished high-resistivity silicon substrates allowed transmittance measurements to determine the IR penetration depth. This information was used to insure that the films subsequently prepared for characterization were optically thick. Such a film was deposited onto a glass slide and characterized by ellipsometry.

Lamellar gratings of 20 µm period, 50% duty cycle and different amplitudes were formed by photolithography and plasma etching in silicon. Then an optically thick Sb layer was thermally deposited on these structures. The subsequent morphology was measured using a step profilometer.

Specular reflectance as a function of incidence angle was measured for the antimony gratings using quantum cascade lasers (QCL) at 9.38 or 6.14 µm wavelengths and 77 K HgCdTe
detector, or a line-tunable CO₂ laser and power meter. In all cases, the laser radiation was p-polarized, i.e. with the electric field vector in the plane of incidence. The grating samples and detector were mounted on the theta and 2-theta parts of a motorized goniometer, respectively. SPP generation was observed as a resonant decrease in the reflected intensity at certain angles.

6.3 Results

Figure 28 presents the complex permittivity spectrum determined from ellipsometry data (solid curves). This is compared with previously published results (symbols) of [85,86] for bulk Sb and [87] for a ~160 nm thick film. All the curves are similar. Our data show that $\varepsilon'$ crosses from positive to negative values at a wavelength of 11.1 μm, as indicated by a vertical line. The crossing point for the Harris data is the same. The crossing points for the Fox [85] and Shkliarevskii [86] data lie on either side, namely at 11.6 and 10 μm, respectively. Vertical line symbols indicate the laser wavelengths used in our experiments. The imaginary part of the permittivity is significantly larger than the magnitude of the real part at CO₂ laser wavelengths, and they are comparable to each other at 6.14 μm. This is in contrast to the usual assumption for ordinary metals at visible wavelengths where $|\varepsilon'| \gg \varepsilon''$ generally holds.
Figure 28: Real part (upper) of permittivity for Sb. Imaginary part (lower). The symbols are from [85-87]. The smooth curves are from the ellipsometry data of this work. Laser wavelengths are indicated by short vertical lines. The long vertical line indicates the plasma frequency.

Drude constants were extracted by fitting Eqs. (2.4-2.5) to the measured complex permittivity data for wavelengths in the range of 15-40 μm. The values obtained are ω_p = 0.134 ± 0.005 eV, ω_τ = 0.060 ± 0.003 eV, and ε_∞ = 105 ± 10. This plasma frequency is 20% larger.
than the frequency at which $\varepsilon'$ is observed to change sign, but the permittivity already deviates significantly here from the Drude like behavior.

The transmittance of two Sb films having thicknesses of 340 and 680 nm was measured, and Eq. (2.16) was used to find the IR penetration depth, which is compared in Figure 29 with values calculated from the measured optical constants using Eq. (2.17). Vertical line symbols indicate the laser wavelengths used in our experiments with gratings. Near a wavelength of 8 $\mu$m, the penetration depth peaks at ~570 nm, which is a factor of 2 smaller than the thickness of the films deposited for ellipsometry and to form Sb gratings (1.15 and 1.19 $\mu$m thick respectively). For this reason, the ellipsometry results are considered to give information mainly on the Sb film with little influence by the substrate.

![Figure 29: IR penetration depth spectrum of Sb as calculated from experimental transmittance of two thin films and from empirical permittivity data. Laser wavelengths are indicated by vertical lines.](image-url)
Figure 30 presents the profiles for the antimony gratings. The period is found to be 21.4 µm, i.e. slightly larger than the nominal 20 micron period of the mask, and this suggests a systematic calibration error in the horizontal scale of the profilometer, since mask dimensions are expected to have high tolerances. Consequently, the nominal 20 µm period is used in all calculations. The grating amplitudes are found to be 0.54, 1.05, and 2.03 µm. The Sb grating duty has been increased (from 50%), and the corners rounded, in comparison with the patterned silicon substrate.

Figure 30: Antimony grating profiles. Grating amplitudes from top to bottom are 1.05, 0.54, and 0.24 µm.
Figure 31: Angular reflectance spectra of Sb gratings at QCL and CO\textsubscript{2} laser wavelengths. Smooth curves are calculated spectra which are shifted vertically for clarity.

Figure 31 presents angular reflection spectra of Sb gratings using two QCL and two CO\textsubscript{2} wavelengths. SPP resonances appear clearly for grating amplitudes exceeding 0.5 \(\mu\text{m}\).
Calculated resonance angles from Eq. (2.6) are indicated by symbols. Theoretical curves fit well with the \( m = 1 \) resonances, especially for the CO\(_2\) laser data. The QCL data are artificially broadened by the several \% band width of these multimode lasers. The fittings have been shifted vertically for clarity. Angular reflection spectra for the uncoated silicon gratings show no resonances. This indicates that the observed resonances are of “resonance type” [4], corresponding to generation of surface plasmons.

The energy decay length \( L_x \) in the direction of SPP propagation, calculated according to Eq. (2.8), is presented in Figure 32 (top) as a function of free-space photon wavelength. For comparison, values for Pd\(_2\)Si (discussed in the previous chapter) are plotted [27]. At CO\(_2\) laser wavelengths, SPPs on antimony have a propagation length approximately 35 times smaller than on Pd\(_2\)Si. The feature near 11 \( \mu \)m for Sb occurs where \( \varepsilon' \) changes sign. Note that the propagation length is similar on either side of the transition.

The characteristic penetration of the SPP electric field into the dielectric (in this case air) and into the conducting film were determined by Eq. (2.9). The 1/e penetration depth of the SPP electric field into the dielectric, \( L_{db} \), or the conductor, \( L_c \), are presented in Figure 32 (bottom) as functions of free space wavelength, for antimony and Pd\(_2\)Si as before. For antimony, the penetration depth into air is approximately twice the wavelength in the CO\(_2\) laser range. It is about a factor of 5 smaller for antimony than for Pd\(_2\)Si. Note that the penetration depths for Sb differ little on either side of the 11 \( \mu \)m sign change for \( \varepsilon' \).
Figure 32: Properties of SPPs on Sb. (upper) Propagation length as a function of free space wavelength. (lower) Penetration depths versus free space wavelength. Upper curves show penetration depth into air while the lower curves show penetration depth into the conductor. Pd<sub>2</sub>Si results are plotted for comparison [27].

Further evidence that surface plasmons are possible for antimony in the wavelength region investigated is obtained by the calculation of surface plasmon modes. Figure 33 (left) gives the surface plasmon electric field modes (Eq. 2.3) based on the measured complex permittivity for an antimony grating with a wavelength in the “normal” bound SPP region ($\lambda = 16.2 \, \mu m$) of the dispersion relation with $\omega < \omega_p / \sqrt{(1 + \varepsilon_d)}$. Figure 33 (right) gives the electric field of the surface plasmon modes calculated again by Eq. 2.3 but this time above the plasma
frequency corresponding to the smallest wavelength measured here (\( \lambda = 6.14 \, \mu \text{m} \)). The surface plasmon fields are still apparent although decay much more quickly in all directions as expected (as seen in Figure 32). This shows that based on the dispersion relation and surface plasmon electric field, surface plasmon modes are still possible at this wavelength even though they decay much more quickly.

![Figure 33: SPP fields on Sb at wavelengths (left) 16.2 \( \mu \text{m} \) and (right) 6.14 \( \mu \text{m} \). Insets show close-up of SPP fields.](image)

Figure 34 gives the difference of the surface plasmon dispersion curve (Eq. 2.1) and the light line, \( k = \omega / c \). The line is from Eq. (2.1) using the empirical permittivity data. The laser wavelengths used in the experiments are indicated by symbols. Since \( \omega_c \) is not small compared with \( \omega_p \), as in the case for usual noble metals, the polariton nature of the dispersion curve, namely the usual inflection near \( \omega = \omega_p / \sqrt{1 + \varepsilon_d} \), is scarcely noticeable except in this
difference spectrum. The positive data define the region of “bound” SPPs corresponding to negative $\varepsilon'$. Our experiment corresponds to “unbound” SPPs.

![Graph](image)

Figure 34: Difference of SPP dispersion curve and light line using empirical permittivity data for Sb. Laser wavelengths used in this work are indicated by vertical lines.

Figure 35 presents the calculated dependence of the resonance spectrum on $\eta_d$. This is the basis for sensing of molecules that might bind to the functionalized surface. The resonance width is independent of $\eta_d$.  

75
6.4 Discussion

The usual condition for bound SPPs is that the real part of the permittivity be negative [30,38], and the usual situation for noble metals in the visible is that $\varepsilon_c' < -|\varepsilon_c'|$. At the laser wavelengths used in this study, which are in the range 6 – 11 microns, the $\varepsilon_c'$ values are slightly positive (Figure 28) and $\varepsilon_c' > |\varepsilon_c'|$. Nevertheless, clear resonances are observed in the angular reflectance spectra (Figure 31) which are attributed to SPPs on Sb since similar measurements on the uncoated silicon gratings yielded no resonances. Sensor applications mainly require the existence of any resonance that is sensitive to changes in the permittivity in the dielectric above the grating. The question of whether the SPP is bound or unbound is irrelevant.
A plot of the spatial field distribution (Figure 33) shows little difference above and below the transition besides the decay lengths in all directions. This is already indicated by Figure 32, where SPP propagation and penetration differ little on each side of the plasma wavelength (~11 µm). For “ideal” metals, $k_z$ is pure imaginary in the bound SPP region and pure real in the unbound region. For Sb, calculations of $k_z$ using the measured permittivity (Eq. 2.2) shows only slow monotonic change and no discontinuities in the real or imaginary part throughout the 2 – 40 µm wavelength region, indicating that SPPs propagate away from the grating but with exponentially decaying amplitude, regardless of the sign of $\epsilon'$. In other words, there is little distinction between “bound” and “unbound” SPP modes for Sb.

For a SPR biosensor with a glass prism and gold at visible wavelengths a refractive index change of $10^{-3}$ can lead to resonance shift of ~0.1° [19]. With a SPR system using Sb gratings at a wavelength of 6.14 µm and a grating period of 20 µm, the same refractive index gives a shift of only ~0.01°. But by decreasing the period to 2.7 µm, the shift increases to ~0.1°. The resonance width is essentially independent of grating period. A potential advantage of a molecular sensor that operates in the IR is the opportunity to operate near characteristic vibrational absorption lines. Then selectivity is enhanced, and dispersion of the refractive index allows a larger index change and hence higher sensitivity.

In summary, this chapter reports the observation of plasmon resonances in the experimental and calculated angular reflection spectrum from Sb grating couplers. These resonances appear even though the photon frequency is above the usual “limiting” SPP frequency. Though all these wavelengths (6-11 µm) were in the range of unbound radiative
SPPs, the resonances are distinct and potentially useful for biosensor applications. Antimony may also be useful for IR plasmon waveguide applications, though the mode confinement is no better than twice the photon wavelength at any frequency. The mode confinement and propagation length are comparable to those of highly doped-Si [27] with carrier concentrations in the range $10^{20}$ to $10^{21}$ cm$^{-3}$. 
CHAPTER SEVEN: MATERIALS FOR THE INFRARED SURFACE
PLASMON RESONANCE BIOSENSOR

7.1 Introduction

A SPR biosensor that operates deep into the infrared (3-11 µm wavelengths) is potentially capable of biomolecule recognition based both on selective binding and on characteristic vibrational modes. A goal is to operate specifically at wavelengths where biological analytes are strongly differentiated by their IR absorption spectra and where the refractive index is increased by dispersion as discussed in Chapter 2. This will provide enhanced selectivity and sensitivity, when biological analytes bind reversibly to biomolecular recognition elements attached to the sensor surface. This chapter investigates potentially useful IR surface plasmon resonances on lamellar gratings formed from various materials with IR plasma frequencies. These include doped semiconductors, semimetals, and conducting polymers. The effect of water on the IR plasmon resonance is also investigated.

7.2 Background

Gratings are well known as couplers between photons and SPPs [30,37]. They function by shifting the incident photon wavevector by integer multiples \( m \) of \( 2\pi/a \), where \( a \) is the grating period. This allows intersection between photon and SPP dispersion curves so that momentum may be conserved during the transition (surface electromagnetic waves travel slower than free
space ones). Grating couplers feature multiple resonances due to the multiple units of grating momentum that may be added. A number of different conductors were considered. We have published theoretical and experimental studies of doped-Si [27,30,33], metal silicides [27,30,34] and the semi-metal antimony [26,33], some of which are discussed in earlier chapters. Also considered here are the semiconductor CuSnS, the semimetals graphite and Bi and the conducting polymer polyaniline.

For ellipsometry measurements, an optically thick sample of Bi was thermally evaporated onto Si substrates as also described for Sb in Chapter 6. A CuSnS film was formed by wet-chemical deposition on on Mo substrates. A commercial high purity graphite wafer 1 mm thick, SPI-3 grade was obtained. All doped-Si wafers were obtained commercially.

Gratings of 20 µm period, 50% duty and different heights were formed by photolithography and plasma etching. For Au and Bi, an optically thick layer was thermally evaporated onto patterned Si as also described for Sb in Chapter 6. The graphite grating was plasma etched directly into the purchased high purity crystalline graphite substrate. CuSnS gratings were formed by wet-chemical deposition on patterned Mo substrates. Gratings were etched from p-type silicon wafers of carrier concentration 6x10^19 and 10^20 cm^-3. A Pd$_2$Si grating was prepared by coating a Si wafer with ~600 nm Pd by e-beam, with the sample then being annealed for four hours at ~500°C with flowing nitrogen to form the silicide. Standard photolithography techniques were used along with an e-beam evaporator to deposit 600 nm of Pd form the grating bars. The wafer was annealed again at ~500°C in flowing nitrogen for 8 hours to complete the formation of the silicide grating. Actual grating heights were determined by a profilometer. Details of the reflectance measurement method are given in Chapter 2.
7.3 Surface Plasmon Hosts

Conductors with plasma frequencies one order smaller than for noble metals are considered in order to obtain good mode confinement in the IR. This requires carrier concentrations two orders smaller. Equivalently, the real part of the permittivity should go negative at a suitable mid-IR wavelength. At the same time, the imaginary part of the permittivity should be sufficiently small so that the resonances are sharp. Figure 36 presents the real part of the permittivity, $\varepsilon'$, from ellipsometry measurements on CuSnS, doped polyaniline [88], Graphite, Sb [26], and Bi as well as doped-Si with relevant carrier concentrations. The wavelength of 10 $\mu$m is indicated by a vertical line. The imaginary part of the permittivity is presented in Figure 37. The curves for Sb and Pd$_2$Si and the lowest concentration of p-Si are reproduced in Figure 36 and Figure 37 from earlier chapters for completeness. Near a wavelength of 10 $\mu$m, Au and Pd$_2$Si have much higher $\varepsilon''$ while the smaller doping concentration of Si have the smallest as indicated. Most of the possible SPP hosts with have an imaginary part, $\varepsilon''$, which is comparable to or higher than the real part suggesting that resonances may be broad. Expected resonance angles and the angular reflectance spectra are calculated using the $\varepsilon'$ and $\varepsilon''$ values according to analytic formulas described in Chapters 3 and 2 respectively.
Figure 36: Real part of the permittivity as measured by ellipsometry for CuSnS, graphite, Bi, Sb, Pd$_2$Si, and p-Si. The curves for n-Si are calculated from the Drude model. The doped-Si carrier concentrations are noted in the legend. The curve for Au is from published data [89,90]. The energy corresponding to 10 µm free space wavelength is indicated.

Figure 38 presents the calculated SPP field penetration depth into water for multiple surface plasmon hosts. This calculated from the permittivity values in Figure 36 and Figure 37 using Eq. (2.9). Near a wavelength of 10 µm (indicated by a dotted line), Au has the largest penetration depth followed by Pd$_2$Si. All semimetals, CuSnS, and polyaniline have penetration depth ~10 µm. The lowest carrier concentration of doped-Si (p-type $10^{20}$ cm$^{-3}$) gives penetration even smaller than 10 µm. This low penetration depth, compared to gold and even Pd$_2$Si, indicates that these materials are more sensitive to refractive index changes in the dielectric from small biomolecules.
Figure 37: Imaginary part of the permittivity as measured by ellipsometry for CuSnS, graphite, Bi Sb, Pd$_2$Si, and p-Si. The curves for n-Si are calculated from the Drude model. The doped-Si carrier concentrations are noted in the legend. The curve for Au is from published data [89,90]. The energy corresponding to 10 µm free space wavelength is indicated.

To more effectively compare the effect of sensitivity to biomolecule thickness, Figure 39 presents the resonance shift for Au, Pd$_2$Si and doped-Si with an increasing thick biomolecule layer. This is an example using a Si prism as a SPP coupler with a wavelength of 9.25 µm. The dielectric background has an index of 1.333 and the simulated biomolecule has an index of 1.35. Shaded boxed indicate the thickness ranges for 10-90% of the full possible shift, with all materials showing more sensitivity to smaller biomolecules than Au. Lower carrier concentration of doped-Si is observed to be the most sensitive to smaller biomolecules. For a functional IR SPR biosensor, a SP host may be chosen to be sensitive to the size range of the biomolecules to be detected.
Figure 38: SPP Field penetration depth into water. The water is assumed real with an index of 1.257.
Figure 39: Resonance shift for Au, Pd2Si and doped-Si as the biolayer thickness is increased. The coupling method is a Si prism and the wavelength is 9.25 μm. The dielectric index is 1.333 and the biomolecule index is 1.35.

7.4 Experiment and Results

Experimental SPR data is presented in Figure 40 for the Pd2Si grating. Using the measured permittivity values, the usual SPP resonance condition for a grating (Eq. 2.6) gives resonance angles of 32.6 and 22.8 at \( \lambda = 9.25 \) μm for the first and third order resonances respectively. These angles are within 2% of the measured angles. The difference is likely due to usual shifts observed for finite grating amplitudes [76]. The \( \lambda = 10.591 \) μm measurement gives similar results. The resonance widths are rather large due to \( \varepsilon'' \) being on the same order as \( \varepsilon' \).

Although the resonances are strong, the penetration depth in water (Figure 38) for metal silicides
is very similar to noble metals making them not as sensitive (Figure 39) as other semiconductors or semimetals.

![Figure 40: SPP resonance data for a lamellar Pd$_2$Si grating of height 0.67 µm, 20 µm period, and 50% duty cycle.](image)

Figure 40: SPP resonance data for a lamellar Pd$_2$Si grating of height 0.67 µm, 20 µm period, and 50% duty cycle.

Figure 41 (top-left) presents optimized calculated resonance spectra for n-Si with different carrier concentrations at the CO$_2$ laser wavelength of 9.250 µm. Evidently, to see a clear resonance, a concentration of at least $10^{20}$ cm$^{-3}$ is required. Figure 41 (bottom-left) presents a measured resonance spectrum for a 1 µm high grating etched in p-Si wafers with a carrier concentration in the range of $1-2 \times 10^{20}$ cm$^{-3}$ [76]. Also presented in Figure 41 (bottom-left) is measurement of a 1 µm high p-Si grating with carrier concentration of $3 \times 10^{19}$ cm$^{-3}$ which shows a structure that seems to indicate the passing of an order. This measurement confirms that
carrier concentrations of this order are not suitable for biosensor applications since no clear resonance is found. These measurements are in reasonable agreement with the calculation.

![Graph](image)

Figure 41: (top-left) Calculated reflectance spectra for n-type Si gratings with varying carrier concentrations. (bottom-left) Measured angular reflectance spectra for a p-type Si lamellar grating of with 1 μm height. (top-right) Calculated reflectance spectra for a CuSnS grating. (bottom-right) Measured angular reflectance spectra for a CuSnS lamellar grating of with 3 μm height. Symbol indicates the calculated resonance angle.

Figure 41 (top-right) shows the optimized calculated resonance for a CuSnS grating at our QCL wavelength of 9.38 μm. The measured angular reflectance spectrum of a 3 μm high CuSnS grating is presented in Figure 41 (bottom-right). A resonance appears in the expected angular position, as indicated by the symbol. The grating height of 3 μm is too large for optimum SPP coupling [37], so that the measured resonances line shape agrees poorly with the optimized calculation.
Reflectance calculation for an optimized graphite grating [37], shows a reasonably sharp and deep resonance (Figure 42 top). The calculated penetration depth for the SPP field into air above the graphite surface is 23 µm at 10 µm wavelength. This is larger than for heavily-doped silicon but smaller than for silicides or noble metals. The measured angular reflectance spectrum for a 0.2 µm high graphite grating is presented in Figure 42 (center). The resonances are very weak but appear near the calculated resonance angles (symbols). The grating height of 0.2 µm is too small for optimum SPP coupling [37], so that the measured resonances line shape agrees poorly with the optimized calculation. The Bi grating shows clear SPP resonances in calculations (Figure 42 top) and in measurements (Figure 42 bottom). The Bi grating amplitude was 1 µm. The same figure shows that a similar situation holds for Sb (seen in more detail in the previous chapter). A 1 µm grating amplitude is close to optimum, so that the measured resonance profile agrees well with the optimized calculation [26]. An optimized reflectance calculation for polyaniline (Figure 42 top) gives a resonance that is deeper and sharper than those for Sb, Bi and Graphite gratings.
Figure 42 (left-top) Calculated reflectance spectra for optimized Graphite, Sb, polyaniline and Bi gratings. The indicated ordering of the curves is the same on both sides of the resonance. (left-center) Measured angular reflectance spectra for a Graphite lamellar grating of with 0.2 µm height. (left-bottom) Measured angular reflectance spectra for Sb and Bi lamellar gratings of with 1 µm height. Symbols represent the calculated resonance angles.
Figure 43: Measured angular reflectance spectra for a Au lamellar grating of with 1 µm height with an attached ZnSe window with and without H₂O filling the gap between grating and window. Curves without noise are calculations.

Water, the usual media in biosensor applications, has considerable dispersion in the IR, and values for $\varepsilon''$ are significant. Hence, it is expected that the resonances will be both shifted and broadened for wet gratings in comparison to dry ones. To investigate this experimentally, a 1 µm amplitude Au grating was prepared. A ZnSe window was attached in contact with the grating. The reflectance from the gold grating was measured before and after the addition of the ZnSe window which should no effects indicating that it is further from the grating than the SPP
mode height is above the grating, and thus it doesn’t need to be taken into account in the calculations. A drop of water placed at the edge of the window flowed by capillary attraction into the gap, providing a uniform layer. The reflected laser intensity was observed to drop by a factor of ~3 due to absorption by water. This drop was used to estimate that the water layer thickness was ~ 10 μm. This estimated water thickness for the wet measurement is on the same order as the wavelength which indicates that Snell’s law does not apply in between any air and this layer. The calculations with no Snell’s law taken into account confirm this by agreeing with the measured resonance angles. Figure 43 presents measured reflectance spectra, both wet and dry. The resonances are labeled by the number of the grating quanta involved. Both initial dry resonances are sharp, but water broadens and shifts them significantly. The experimental observations agree with calculations.

Figure 44 (left) presents the extinction coefficient of water [91]. The wavelength 9.25 μm is indicated in Figure 44 (left) by an arrow. An extinction coefficient nearly an order of magnitude smaller is found at 3.9 μm. Figure 44 (right) presents a calculated resonance spectrum for the wet conditions in Figure 44 (right) but for at 3.9 μm. The resonance is sharp. The range 3.5 – 5.5 μm is identified as that best suited for an IR SPR biosensor with water due to it having the lowest extinction coefficient in this LWIR region. It is known that many proteins have an absorption line near 3.4 μm due to the H-C bond [92] which is near enough to this range that the extinction is still relatively low. Choosing an operational wavelength slightly larger than 3.4 μm will also take advantage of the increased index on the long wavelength side of this mode and thus have increased sensitivity. If D₂O is used as an bioanalyte carrier instead of H₂O, the best
suited range of extinction coefficients is found between $4.5 - 8 \, \mu m$ [93]. Hence, the choice of using H$_2$O or D$_2$O as an analyte carrier depends on the IR region where vibrational modes of biomolecules are expected.

![Figure 44](image)

Figure 44  (left) Extinction coefficient of water in the IR from [91]. The wavelength used to measure the gold grating in water is indicated by an arrow. The wavelength range with the smallest extinction coefficient for water in the mid-IR is indicated. (right) Calculated resonance spectrum for a Au grating with water at 3.9 \( \mu m \).

### 7.5 Summary

Calculated and experimental SPP resonances on semiconductor, semi-metal and conducting polymer gratings in the IR were presented. All show reasonable prospects as SPP hosts in the IR with sufficient mode confinement for sensor applications. Wetting the grating shifts and broadens the SPP resonances significantly at 9.25 \( \mu m \). To maintain sharp SPR resonances, the ideal range for an IR SPR biosensor would be $3.5 - 5.5 \, \mu m$. To optimize the SPR biosensor system, the liquid utilized to carry analytes must be chosen such that it has low extinction in the wavelength region being investigated.
CHAPTER EIGHT: GOLD-BLACK

8.1 Introduction

Metal-black nano-structured conducting films have been exploited as broad-band surface absorbers for bolometers [23-25]. This work considers the effect for this application of hardening of gold-black via polymer infusion and the possible correlation of IR absorption to the characteristic length scales of the films. Also presented are investigations of the plasmon resonance characteristics of gold-black, which has potential to increase the efficiency of thin film solar cells via resonant scattering and field enhancement.

Metal blacks have been investigated for their optical properties since the 1930’s [22]. Deposition by evaporation in an inert gas at tenths to tens of Torr has followed the method of Harris [94-98] with little change. One objective of this work was to develop an absorber for an innovative MEMS-based bolometric infrared imaging array detector with high frame rates.

Metal blacks are produced in a low-vacuum process, resulting in a porous nano-structured metallic film having a broad particle-size distribution. The morphology depends on the pressure of the inert gas in the evaporation chamber, the deposition rate, and the temperature of the substrate [22]. A correlation between the absorptivity of gold black and the resistivity of the thin films has been exploited [99] to verify the expected properties of as-grown films. Here the possibility of a correlation between absorption and the particle size distribution is investigated.
Silicon has low absorption due to its indirect gap, such that usual solar cells require ~100 micron thickness to capture the incident solar irradiation, but thin films would be preferred for economy and weight. Small metal particles have potential to improve the efficiency of thin-film solar cells via the scattering and field enhancement. Photocurrent gains up to 10 x have been reported [100,101]. Metallic scattering centers increase the effective optical path length in thin films. The scattering cross section peaks at the plasmon resonance frequency, where there is also an enhancement in field strength. The resonance depends on particle size, an effect exploited for centuries to produce stained-glass windows. This work reports initial investigations of particle size-dependence of optically-excited plasmon resonance in gold blacks.

8.2 Experimental Methods

Gold-black is produced here by thermal evaporation of gold onto DSP silicon substrates in a chamber that has been back-filled with 1-2 Torr of inert gas, either nitrogen or helium. The bell chamber setup used can be seen in Figure 45 (left). Samples are mounted on a copper plate, which is attached to a thermoelectric cooler. A thermoelectric cooler is attached to a large copper heat sink with coolant transported through the chamber for lower temperatures. Once the chamber has obtained pressure < 10^{-4} Torr, the desired pressure is reached with an inlet flow of the inert gas, usually on the order of 1 Torr. After the desired pressure is reached, the thermoelectric cooler is used to cool the samples. The depositions then are completed under with evaporation current specific to each sample (see the respective tables). The films are sufficiently
thin, approximately 50 nm, to allow some transmission of an optical beam. Figure 45 (right) shows a typical Au-black film.

Figure 45: (left) Bell chamber showing thermoelectric cooler attached to heat sink (top) across from the electrodes and molybdenum boat (bottom). (right) Gold black sample deposited on silicon compared to a standard gold-coated piece of silicon.

Infrared absorption was determined from transmittance and reflectance spectra collected using a BOMEM DA8 Fourier transform spectrometer as described in chapter 2. The figure of merit (FOM), defined as

\[ FOM = 1 - T - R, \]  

(7.1)

is a measure of absorbance. It is not exactly the same as absorbance, however, since the reflectance was completed at 30° angle of incidence at not normal incidence. Due to this, FOM values can range between -1 and 1.
Scanning electron microscope (SEM) images were collected on various instruments at UCF, EMSL and AFRL. A discrete wavelet analysis was performed on each image using a Morlet wavelet [102,103]. The wavelet transform was calculated for each row of each image. The wavelet transform provides a map of the power present at all wavelengths at different regions of the image, or in this case at different locations within each image row. The wavelet power was integrated along the image row and then sum the power for all rows because we are interested in the overall wavelength power distribution, not spatial variations within the images. The amplitude of the wavelet spectrum is in arbitrary units.

SPR data has been collected using a set-up (Figure 46) similar to that of earlier SPR experiments (Figure 8). A cylindrical BK7 prism was used as an SPP coupler. Glass substrates with deposited gold black films are placed on the back of a prism with glycerine used an index-matching “glue”. As with earlier surface plasmon experiments, a detector is placed at the $2 \theta$ angle from the source. The source is either a Ti:Sapphire laser ($\lambda = 800$ nm) or a Helium-Neon laser which passes through a prism polarizer and chopper. The chopped reflected signal will be detected by a Si diode and synchronously amplified. The goniometer is manually rotated with a Labview program reading the amplified data in real time.
Figure 46: Setup used for Au-Black SPP experiments. Pictured is the goniometer setup used. Laser source originates from the left, passing through a prism polarizer and chopper. An optics dial is used as the goniometer (right) and is manually rotated along with the silicon detector (top).

Photoelectron Emission Microscopy (PEEM) was used to characterize the spatial distribution of the plasmon resonances. PEEM used a near infrared laser (below the work function of gold (5.1 eV), or a Hg lamp, to excite plasmon resonances. A cooled CCD camera records photo-electron emission from the samples. The Hg arc lamp uses band-pass filters to cover the 400-800 nm range in 50 nm wide steps. Neutral density filters and a calibrated detector allowed us to control the photon fluence within each band.

8.3 Preliminary Results

Initial experiments determined the parameters of interest and their useful ranges, resulting in samples designated series “A” and series “B”. Gold black samples were created using
Nitrogen gas during the deposition process with the parameters found in Table 5 (series “A”).

The deposition process for series “A” was completed at room temperature during the deposition process. Transmission and Reflectance data in the mid-IR for these samples were completed and the FOM was calculated according to Eq. 1. It is noted that the gold black sample made at the highest pressure here had low transmissivity but also the largest reflectivity. Table 5 shows the empirical FOM found from the transmission and reflection measurements at 100 and 400 cm$^{-1}$.

The most absorbing film of the five is sample A4 which has, in general, the lowest reflectivity out of the group and the 2$^{nd}$ lowest transmission. The difference between sample A5 and A4 is a difference in relative current during evaporation. The two parameters in the case of data presented here are pressure of nitrogen in the bell chamber and current used for the deposition. This is an early indication that higher currents and higher pressure during deposition generally help create more absorbing samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pressure (Torr)</th>
<th>Relative Current</th>
<th>FOM @ 100 cm$^{-1}$</th>
<th>FOM @ 400 cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.2</td>
<td>4.5</td>
<td>0.21</td>
<td>-0.18</td>
</tr>
<tr>
<td>A2</td>
<td>0.2</td>
<td>3.5</td>
<td>0.04</td>
<td>-0.38</td>
</tr>
<tr>
<td>A3</td>
<td>0.5</td>
<td>3.5</td>
<td>0.15</td>
<td>-0.42</td>
</tr>
<tr>
<td>A4</td>
<td>0.5</td>
<td>4.5</td>
<td>0.70</td>
<td>0.73</td>
</tr>
<tr>
<td>A5</td>
<td>0.75</td>
<td>4.5</td>
<td>0.59</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Sample A4 is found to be the most absorbing out of series “A” while sample A5 was the 2$^{nd}$ most absorbing as seen in Table 5. The SEM data in Figure 47 shows cloud shaped structures for these two samples. The structures in sample A4 (the more absorbing film) are approximately
one order of magnitude larger than those in sample A5. SEM images of samples A1-A3, all lowly absorbing, show different structures with none showing the cloud-like structures observed with A4 and A5. From these initial considerations, a correlation could be found between larger cloud-like clusters of gold particles and higher absorption.

Figure 47: SEM data for gold black samples in table 1. Clockwise from top-left corner are samples A1-A5.

Gold black samples were then created using Helium gas during the deposition process with the parameters found in Table 6 (series “B”). Only select samples in this series with the most positive results are shown. The substrates were cooled using the thermoelectric cooler. The temperature was allowed to stabilize before the deposition was initiated. As before, Transmission and Reflectance data in the mid-IR for these samples was used to calculated the FOM. Repeating reflectivity or transmission spectra show slight variations showing some dependence on sample positioning. Figure of merit is calculated at the wavenumbers 100 and 400 cm\(^{-1}\) as
before. This data is presented in Table 6. Corresponding SEM images are shown in Figure 48Figure 49. Figure 48 shows two SEM images from different regions of sample B6 which gives clusters that vary but seem to be consistent within these regions. In general, the larger clusters have stronger absorption (samples B24 and B42). The best absorbing sample from this group was B29 contains clusters ~1 μm in size similar to the earlier sample A4. The weaker absorbing samples (especially for higher wavenumber) are B43 and B45, which have the smallest particle sizes (<1 μm).

Table 6: Select Gold black “B” samples deposited with a corresponding helium pressure, evaporation current, initial substrate temperature and measured FOM.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pressure (Torr)</th>
<th>Relative Current</th>
<th>Initial Substrate Temp. (°F)</th>
<th>FOM @ 100 cm⁻¹</th>
<th>FOM @ 400 cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>B6</td>
<td>1</td>
<td>3</td>
<td>35</td>
<td>0.11</td>
<td>0.71</td>
</tr>
<tr>
<td>B24</td>
<td>1.3</td>
<td>2.62</td>
<td>36</td>
<td>0.3</td>
<td>0.45</td>
</tr>
<tr>
<td>B29</td>
<td>2</td>
<td>3</td>
<td>37</td>
<td>0.39</td>
<td>0.45</td>
</tr>
<tr>
<td>B39</td>
<td>1.3</td>
<td>2.7</td>
<td>51</td>
<td>0.03</td>
<td>0.5</td>
</tr>
<tr>
<td>B40</td>
<td>1.3</td>
<td>2.7</td>
<td>37</td>
<td>0.11</td>
<td>0.51</td>
</tr>
<tr>
<td>B41</td>
<td>2</td>
<td>2.58</td>
<td>40</td>
<td>0.23</td>
<td>0.63</td>
</tr>
<tr>
<td>B42</td>
<td>2</td>
<td>2.58</td>
<td>34</td>
<td>0.31</td>
<td>0.77</td>
</tr>
<tr>
<td>B43</td>
<td>1.3</td>
<td>2.38</td>
<td>32</td>
<td>0.17</td>
<td>0.36</td>
</tr>
<tr>
<td>B44</td>
<td>1.6</td>
<td>2.4</td>
<td>31</td>
<td>0.26</td>
<td>0.6</td>
</tr>
<tr>
<td>B45</td>
<td>1.6</td>
<td>2.4</td>
<td>33</td>
<td>0.17</td>
<td>0.36</td>
</tr>
</tbody>
</table>
Figure 48: SEM data for gold black samples B6 (see Table 6). Two different regions of the same sample are presented.

Figure 49: SEM data for gold black samples in Table 6. Left to right are samples B24, B29, B39, B41 (top row) and B42-B45 (bottom row). No clear SEM image of B40 was obtained.
8.4 SPR Measurements on Au-Black

SPR data has also been collected on Au-black samples from series “A” and “B”. A surface plasmon reflectance measurement experiment was setup with a prism and He-Ne laser similar to that described for the prism experiments discussed in chapter 4. Au-black samples were deposited on glass slides simultaneously with the silicon substrates which were attached to a cylindrical BK7 prism with glycerin. It is assumed that the films on Si substrates that have characterized are similar to those on glass substrates.

An attempt was made to measure the permittivity of Au-black films via ellipsometry, but the rough porous surface caused too much scattering. A different method would be needed to determine the permittivity of Au-black since this knowledge of this parameter can greatly determine the films usefulness. Experimental Au-black SPR data fitted using the thin film theory presented in Eqs. 4.1 – 4.5 to obtain the film thickness $d$ and the volume fraction of Au to Au-Black $f$ which takes values from 0 to 1 using the Bruggeman formula. This well known formula has been used successfully to fit SPR data on electrochemically deposited Au-Black in order to obtain the two parameters in Reference [21]. The Bruggeman formula with an effective Au-Black permittivity $\varepsilon_{\text{Au-Black}}$ is

$$
(1 - f) \frac{\varepsilon_{\text{air}} - \varepsilon_{\text{Au-Black}}}{\varepsilon_{\text{air}} + 2\varepsilon_{\text{Au-Black}}} + f \frac{\varepsilon_{\text{Au}} - \varepsilon_{\text{Au-Black}}}{\varepsilon_{\text{Au}} + 2\varepsilon_{\text{Au-Black}}} = 0 .
$$

(7.2)

It is noted that this theory is not accurate in the region of low $f$. Solving for $\varepsilon_{\text{Au-Black}}$ and retaining the real solution of the quadratic equations gives an effective permittivity of the form
where

\[ C_1 = 2 / f, \tag{7.4} \]

\[ C_2 = 1 + 2(f - 1) / f - \varepsilon_{Au} (f - 1) / f - 2\varepsilon_{Au}, \tag{7.5} \]

and

\[ C_3 = -\varepsilon_{Au} / f. \tag{7.6} \]

Using the thin film method for fitting experimental SPR data for Au-Black along with the Bruggeman theory, knowledge of film thickness, composition and effective permittivity can be obtained. With a general understanding of \( \varepsilon_{Au-Black} \), films can be developed more specifically to be more absorbing.

SPR measurements were completed on sample B6 with a He-Ne laser. Visibly, the gold black coating was dark although uneven. Two different, but visually identical spots were studied. Figure 50 (left) shows a single sharp resonance while Figure 50 (right) shows a possible double resonance indicated by the arrows. The double resonance angles could indicate two distinct film thicknesses regions at the point the light was incident onto the sample. The difference in broadness may also indicate that the sample is much thicker at the 2\(^{nd}\) spot than the 1\(^{st}\) spot. The blue curves in Figure 50 are the fitted curves using the Bruggeman theory from above. Fittings of the SPR for both spots are found in Table 7. In the 2\(^{nd}\) spot, the fitting only considered the first resonance. The main difference between the fitting on the SPR measurements of the two spots is the film thickness which may indicate the observed shifting between the two resonance spectra.
Figure 50: SPP reflectivity data for Au-Black sample B6. The different colored curves are multiple data sets of the same spot on the sample. (left) and (right) are measurements of different spots on the same sample ~5 mm apart. Note that different spots on the same non-uniform sample give very different resonance line shapes and positions, supporting our hypothesis that SPP spectroscopy is sensitive to film condition.

Table 7: Fitting of SPR Au-Black from sample B6 curves by the Bruggeman formulation (Eqs. 7.2 – 7.6). The wavelength is 632.8 nm and the Au permittivity is \(-9.6 + 1.1i\) [90].

<table>
<thead>
<tr>
<th>SPR.</th>
<th>d (nm)</th>
<th>(\varepsilon_{\text{eff}})</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 50 (left)</td>
<td>98±5</td>
<td>(-3.5 + 0.65i)</td>
<td>0.67±0.02</td>
</tr>
<tr>
<td>Figure 50 (right)</td>
<td>120±10</td>
<td>(-3.0 + 0.72i)</td>
<td>0.65±0.02</td>
</tr>
</tbody>
</table>

SPR measurements were completed on sample A4 with a NIR wavelength of 800nm which are presented in Figure 51. The arrows in the figure indicate possible SPP resonances. The multiple resonances at this wavelength indicate non-uniformity of the film. Fittings using this data to determine the parameters of the film will be much more complex in this case than those found in Figure 50.
The effects of sample morphology are revealed by the change in the angular position of the SPP excitation peak, the appearance of multiple resonances and their line shapes. The effect of the nanostructure of the gold is to broaden and shift the resonance peak. The SPP resonance spectrum for a gold-black sample in Figure 50 contains a line shape that is clearly wider and the peak occurs at a larger angle than for corresponding optical frequency on smooth gold film (Figure 18). Figure 51 shows that multiple resonance are possible due to the complicated structure of the film, which complicates analysis of the optical constants. Further analysis of Au-black by surface plasmon resonance will require the deposited films to be uniform which may prove to be a difficult task. However, the corrugated surface may act as a grating exciting multiple modes simultaneously (Figure 51) which will be discussed in the next section. Future work will depend greatly on depositing films with a thickness even to the order of 1 nm or better.
8.5 Full Factorial Results

After initial gold-black experiments, a two level full factorial optimization scheme, including polymer infusion, was followed to determine the conditions that produce maximum absorbance, producing the samples in series “C”. This protocol is the most statistically sound and economical approach to optimization when underlying physics is poorly understood.

Parameters chosen to be varied in the full factorial experiments were He pressure, evaporation current, and substrate temperature. Each parameter took one of two values. In addition, after characterizing these samples, they were infused with polymer to two different levels of saturation. With 4 parameters, we have $2^4 = 16$ different combinations. Four intermediate points were also included to reveal curvature. A matrix of experiments was set up so that every combination of parameter values in the scheme is completed in random order to avoid systematic errors. The sample parameters of series “C” are located in Table 8. The location in parameter space that optimized the films (as characterized by a figure of merit to be defined) and correlations between parameters are then discovered.
Table 8. Matrix of experiments in two-level full factorial optimization of gold black. The variables are He pressure (P), substrate temperature (T), boat current (I), and level of polymer infusion. High (+), low (-), and intermediate (*) levels are indicated. The final column shows which samples were also characterized by PEEM. Sample C02 was destroyed before it could be measured. Its conditions were duplicated in another sample. Bold samples are those with the best FOM.

<table>
<thead>
<tr>
<th>sample</th>
<th>P</th>
<th>T</th>
<th>I</th>
<th>Polymer</th>
<th>PEEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>C01</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>X</td>
</tr>
<tr>
<td>C03</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>C04</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>C05</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>+</td>
<td>X</td>
</tr>
<tr>
<td>C06</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>C07</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>C08</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>C09</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>X</td>
</tr>
<tr>
<td>C10</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>C11</td>
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Infrared FOM was determined at 150 and 600 cm\(^{-1}\) wavenumbers, corresponding roughly to the THz and long wave IR (LWIR) bands. The results are summarized in Figure 52. The samples are numbered in the order they were prepared. The FOM values at 150 and 600 cm\(^{-1}\) are strongly correlated. A tendency of polymer infusion to reduce the FOM at 600 cm\(^{-1}\) is observed, but this is less significant at 150 cm\(^{-1}\). For the samples with highest FOM there is a slight
tendency for polymer infusion to increase the figure of merit slightly. Mid-point measurements allow us to conclude that the dependence of FOM on each variable, and as well as interactions between variables, have strong curvature.

Figure 52: Figures of merit at THz and Long-wave IR frequencies for gold-black samples of Table I. Solid (open) symbols indicate values after (before) polymer infusion.

Figure 53 presents SEM images of two of the gold black samples from Table 8. The metallic particles are arranged in interconnected groups with a broad-range of characteristic length scales or spatial wavelengths. These two images were chosen for presentation because of the large difference in their characteristic length scales.
Figure 53: SEM images of sample C04 (left) and C09 (right). Both images have 25 micron field of view.

Figure 54 presents the wavelet analysis of SEM images for C04 and C09 with 50 micron field of view. The wavelet power spectrum is characterized by a series of overlapping peaks. The upper wavelength cutoff is determined by the maximum dimension of the image. For two images with the same magnification, the lower limit is a quantitative measure of the minimum characteristic length scale in the image. The minimum characteristic length scale as defined as the point where the power is half the maximum value.
Figure 54: Wavelet analysis of SEM images for samples C04 and C09. The images had 50 micron field of view. The amplitude scale is normalized.

Figure 55 plots FOM values at THz and LWIR wavelengths as a function of the minimum length scale from the wavelet analysis of images with 50 micron FOV. At each wavelength, the FOM values appear in roughly two groups. Within each group there is no clear correlation between FOM and length scale. However considering both groups simultaneously, there appears to be a slight tendency for the high FOM points to be clustered at low length scale and vice versa. In other words, there may be a tendency for samples with smaller length scales to give higher absorbance. This is the opposite of the preliminary gold-black results but the wavelet analysis of the series “C” samples is more complete and the FOM as presented in Figure 55 gives the most complete picture yet giving more credibility to this result than earlier results.
Figure 55: Infrared figure of merit as function of minimum characteristic length scale for gold-black.

Figure 56 presents PEEM images for Hg-arc-lamp illumination of samples C01, and C13. The image records the spatial position of emitted photoelectrons. The bright areas are “hot spots”, where plasmon resonances facilitate photoemission since the wavelengths are well below the work function for gold (~5.1 eV). These initial PEEM studies were on samples designed as IR absorbers. For plasmonic solar cell enhancement, the substrate coverage would need to be much lower. Still these observations give some indication of what effects one might expect. In Figure 56 (right), the lower left part of the sample has been modified by a focused ion-beam mill (FIB) to make a marker for alignment. First, it is noted that the modified surface has a noticeably different morphology in the SEM image and is less bright in the PEEM image, showing that it has less plasmon activity. Second, the distribution of bright-white hotspots in the
PEEM image is less dense in the modified region than one might expect from the distribution of comparable structures in the SEM image.

![PEEM images of samples C01, and C13 (FOV = 150 microns.)](image)

Figure 56: PEEM images of samples C01, and C13 (FOV = 150 microns.)

Figure 57 presents wavelet analysis for the PEEM images of Figure 56. The symbols indicate the minimum length scale from the SEM images (50 micron FOV). It is noted that though the two samples have significantly different morphology and particle size distributions, the wavelet analysis shows that the plasmon resonances first appear at nearly the same length scale, namely at about 5 microns. This is true even though sample C13 has comparatively few structures as small as 5 microns. This size is comparable to the size of the hot spots in Figure 56. These results tentatively suggest that there is a certain minimum for the excitation of plasmon resonances, and that this minimum which may be larger (as in in the case of C01) than the
minimum size in the sample. Above this minimum, however, there is a broad range of length scales that give rise to plasmon-assisted photo-emission.

![Graph](image)

Figure 57: Wavelet analysis of the PEEM spectra of Figure 56. Symbols indicate the minimum length scale observed in the SEM image.

Figure 58 present histograms of the images from Figure 56 for samples C01 and C13. The higher concentration of bright hot spots for C01 is revealed as a bump at the highest intensity level. In principle, the ratio of this bump to the area under the lower intensity part of the curve might be used as a measure of hot-spot density in properly controlled experiment.
Figure 58: Histograms for PEEM images of samples C01 (left) and C13 (right).

Figure 59 presents preliminary wavelength dependence results. The field of view is 150 microns. The two laser wavelengths are not very different, and consequently, the hot-spot distribution for the two images is nearly identical. Nevertheless, the image for the longer wavelength shows more contrast, i.e. the hot-spots are brighter relative to the background. It is suggested here that this is because the wavelength is now closer to the surface plasmon resonance wavelength for gold (~500 nm).

Figure 59: Gold black sample (C13) illuminated by a laser at two different wavelengths, (left) 370 nm and (right) 420 nm.
8.6 Discussion

The results presented here suggest that hardening of gold black tends to lower the LWIR FOM somewhat, while this characteristic is less affected in the THz spectral range. Our hypothesis that the IR absorbance would be correlated with the characteristic length scale of the gold-black films is poorly supported by experiment. The observation of photoelectron emission from gold-black samples for wavelengths well below the work function of gold (5.1 eV) suggests that the emission occurs due to the field enhancement at the plasmon resonances. The structured Au-black films appears to be able to support plasmons with incident light coupling to the corrugated surface as seen by PEEM and SPP reflectance experiments. Thus, there is potential for similar useful effects in to enhance the efficiency of solar cells. The broad range of length scales that contribute significantly to the plasmon-assisted photoemission supports the suggestion that gold black may be a suitable material for plasmon-resonance enhancement of solar cell efficiency over the broad solar spectrum.
CHAPTER NINE: CONCLUSIONS

This dissertation work focuses on the extension of the use of surface plasmons into the IR which has numerous advantages for the biosensor and waveguide applications. IR surface plasmons are investigated based on optical coupling techniques for various metal, semiconductor and semimetals.

An approximate analytic formula for use in the design of SPP grating couplers is presented here based on empirical data for Ag lamellar gratings in the IR. This approach relies on an impedance modulation parameter, which has been determined empirically by fitting the measured coupling of photons to SPPs at 6-11 μm wavelengths. Without an accurate theory for the dependence of the impedance modulation parameter on wavelength, material, and grating amplitude, a phenomenological dependence must be established so that the approach may be applied widely to the optimization of grating couplers. Future investigations would involve varying the grating period and material to determine how the impedance modulation parameter changes under these different conditions.

Hemicylindrical prisms where also investigated as IR surface plasmon couplers. Experimental reflectance data in the LWIR using these prisms shows Fabry-Perot oscillations that can be explained by the high Q cavity formed between the two curved surfaces of the prism. These oscillations obscure the resonance and are the main disadvantage of hemicylindrical prisms for our IR biosensor application which leads to the consideration of the triangular prism as an SPP coupler, which may be explored in future work.
Silicon based materials were characterized and the ideal ranges of these materials were determined for SPP applications. The characterization of metal silicides shows they are more suitable for SPP applications at photon wavelengths in the range 5 to 100 µm than are metal films due to better mode confinement while maintaining an acceptable propagation length. Doped-Si with carrier concentrations of $10^{18}$-$10^{19}$ cm$^{-3}$ is best suited for SPP applications at 50 to 200 µm wavelengths, i.e. the THz spectral range. The suitable SPP application range for doped-Si with higher carrier concentrations becomes increasingly comparable to metal silicides. The investigation of plasmonic silicon-based materials is relevant due to their inherent CMOS compatibility.

The observations of plasmon resonances in the experimental and calculated angular reflection spectrum from Sb grating couplers was reported. These resonances appear even though the photon frequency is above the usual “limiting” SPP frequency. Though all these wavelengths (6-11 µm) were in the range of unbound radiative SPPs, the resonances are distinct and potentially useful for biosensor applications. Antimony may also be useful for IR plasmon waveguide applications, though the mode confinement is no better than twice the photon wavelength at any frequency.

Calculated and experimental grating-coupled SPP resonances were also reported on Pd-silicide, semiconductors (doped-Si and CuSnS), semi-metals (Bismuth and Graphite) and a conducting polymer (Pолyaniline) in the IR. Bismuth shows resonances even in the unbound “radiative” SPP range similar to that of Sb. Doped-Si gratings show a resonance-like structure in wavelength range investigated (near 10 µm) only if the carrier concentration is at least $\sim 10^{20}$ cm$^{-3}$. All show reasonable prospects and may also be exploited as SPP hosts in LWIR.
SPR biosensors since characteristic vibrations should yield better specificity and tighter mode confinement. Future work will included measuring reflectance spectra for all materials using gratings with a height closer to the optimum scenario to better characterize the resonances.

The IR SPR biosensor application was investigation using gold gratings with a H₂O layer as a potential bioanalyte carrier. Wetting the grating shifts and broadens the SPP resonances significantly at 9.25 μm. To maintain sharp SPR resonances, the ideal range for an IR SPR biosensor would be 3.5 – 5.5 μm. To optimize the SPR biosensor system, the liquid utilized to carry analytes must be chosen such that it has low extinction in the wavelength region being investigated. Future work in the development of this sensor will include reflectance experiments of gratings with water in the optimum wavelength range with a source and grating specifically chosen and developed respectively for this range.

Nano-structured Au-black films were investigated as IR absorbers and possible solar cell enhancers. The structured Au-black films appears to be able to support plasmons with incident light coupling to the corrugated surface as seen by PEEM and SPP reflectance experiments, and with this excitation confirmed, there is potential for similar useful effects to enhance the efficiency of solar cells. The broad range of length scales that contribute significantly to the plasmon-assisted photoemission supports our suggestion that Au-black may be a suitable material for a plasmon-resonance enhanced solar cell with efficiency over the broad solar spectrum.
APPENDIX A: SEM OF METAL SILICIDES
Figure 60: SEM of Ni-Silicide
Figure 61: SEM of Pd-Silicide
Figure 62: SEM of Pt-Silicide
Figure 63: SEM of Ti-Silicide
APPENDIX B: XRD OF METAL SILICIDES
Figure 64: XRD of Ni-Silicide
Figure 65: XRD of Pd Silicide
Figure 66: XRD of Pt-Silicide
Figure 67: XRD of Ti-Silicide
REFERENCES


[38] H. Raether, Surface Plasmons on Smooth and Rough Surfaces and on Gratings (Springer, New York, 1988).


