Tunable plasmonic structures for terahertz frequencies

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I certify that all material in this thesis which is not my own work has been identified and that no material has previously been submitted and approved for the award of a degree by this or any other University.

Signature:..........................
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Publications

The work in this thesis is, in part, based on the following publications:

Journal articles:


Conference papers:


Abstract

The terahertz frequency range is a relatively unstudied region of the electromagnetic spectrum. However, with the emergence of numerous applications for terahertz light in diverse areas such as security scanning, biological imaging, gas spectroscopy and astrophysics, there has been considerable recent growth in the volume of research activity in this area. The studies presented in this thesis aim to introduce the physics of surface plasmons to the terahertz frequency range, and on the way to use some of the unique capabilities of terahertz spectroscopy to try and find new information about fundamental surface-plasmon based electromagnetic structures.

Four distinct experiments are described in this work, all of them underpinned by the technique of terahertz time-domain spectroscopy (Chapter 2). This is a very powerful and adaptable spectroscopic method which allows us to measure the electric field of pulsed terahertz radiation as a function of time. This in turn allows us to directly extract both phase and amplitude of the terahertz light as a function of frequency, over a broad frequency range. Furthermore, this method of terahertz spectroscopy can be combined with photoexcitation pulses of visible/NIR light which can be used to make dynamic changes to the properties of materials in the terahertz beam.

The first experiment reported (Chapter 3) measures the propagation of coupled surface plasmons in a resonant slit cavity. We use terahertz time-domain spectroscopy to determine the characteristics of the cavity resonances in a semiconductor slit near the surface plasma frequency of the material, where we are able to measure very large red-shifts in the frequency of the cavity resonance. By considering the phase information which can be extracted directly from time-resolved terahertz measurements we are able to link the behaviour of the resonances to the propagation characteristics of the surface plasmon modes inside the slits.

The second experiment (Chapter 4) is a more direct measurement of surface plasmons, propagated over the surface of a semiconductor wafer. We show that the electric field of the surface plasmon is confined to a subwavelength region around the surface, and that the confined field is useful for spectroscopy of very thin layers above the surface. We are able to measure films with thickness less than \(1/600^{th}\) of the wavelength of the terahertz light.
After these two experiments with confined semiconductor surface plasmons we move on to a pair of experiments looking at terahertz surface modes mediating the transmission of light through holes in metal films. In the initial experiment (Chapter 5) we use the time-domain data from terahertz spectroscopy to determine the role that surface mode lifetime plays in modifying the amplitude and width of Extraordinary Optical Transmission (EOT) resonances, which arise from the periodicity of a hole-array lattice. By changing the temperature of the lossy dielectric semiconductor substrate we are able to modify the surface mode lifetime, and link this to the resonant transmission characteristics.

In Chapter 6 we extend the hole array EOT experiment by making dynamic changes to the propagation of the surface mode which mediates the transmission. This is achieved by photo-exciting the semiconductor substrate inside the holes and forming a thin layer of material with high charge carrier density on the surface. Interaction of the surface mode with the photoexcited region quenches the resonant transmission. We show that by changing the hole size so that the surface-mode mediated transmission pathway predominates in the spectrum it is possible to use optical pulses to modulate the transmission of terahertz radiation with very high efficiency.

In the conclusions (Chapter 7) we link together some of the insights and inferences which can be drawn from the above results, as well as evaluating the efficacy of the experimental and simulation methodology.
Definitions

Abbreviations

• **SPP / SP**: Surface Plasmon Polariton / Surface Plasmon
• **THz-TDS**: Terahertz Time-Domain Spectroscopy
• **FEM**: Finite Element Model
• **EOT**: Extraordinary Optical Transmission
• **FP**: Fabry-Pérot

Symbols

Other symbols are used in the text, but the following are assumed throughout.

• $t$: Time
• $\omega$: Angular frequency
• $\nu$: Frequency
• $\lambda$: Wavelength
• $k$: Wave-vector
• $k_{SP}$: Surface plasmon wave-vector
• $L_{SP}$: Surface plasmon decay length
• $E$: Electric field
• $H$: Magnetic field
• $c$: Speed of light in vacuum
Wavelength ranges

At various points a range of wavelengths is referred to by a name; although these names are often loosely defined, in this thesis they fit in to the ranges below.

- **Radio (RF):** $\lambda > 0.1$ m
- **Microwave, Gigahertz (GHz):** $0.1$ m $> \lambda > 1$ mm
- **Terahertz (THz):** $1$ mm $> \lambda > 30$ $\mu$m
- **Infrared (IR):** $10$ $\mu$m $> \lambda > 750$ nm
- **Near-Infrared (NIR):** $1.5$ $\mu$m $> \lambda > 750$ nm
- **Optical:** $3$ $\mu$m $> \lambda > 350$ nm
- **Visible (Vis):** $700$ nm $> \lambda > 380$ nm
- **Ultraviolet (UV):** $\lambda < 380$ nm
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Chapter 1

Introduction

Summary

In this chapter we introduce the terahertz frequency range (which is considered in more
detail in Chapter 2), and the basic physics of surface plasmons. We propose confined
terahertz surface plasmons supported on semiconductors and briefly consider methods of
coupling free-space radiation to surface plasmons. We consider applications for surface
plasmons, including in high-sensitivity spectroscopy and subwavelength guiding. We look
at two structures which support surface plasmons, and the role which surface modes play
in some transmission enhancement phenomena in those structures. Finally we give an
introduction to the techniques of finite element modelling which are used extensively in
this thesis.

1.1 Motivations for this Thesis

The purpose of the work presented in this thesis is to explore the interesting physics
of surface plasmons at terahertz frequencies, particularly in structures and materials
that can be ‘tuned’ in some way to alter their electromagnetic properties. One goal
is to introduce some of the advantages of surface plasmon photonics to the terahertz
frequency range, where they might find applications in improving the efficacy of
low-frequency spectroscopic measurements. Another goal is to side-step some of the limitations of studying surface plasmons in the optical range, such as the constraints caused by the immutability of material parameters and by manufacturing challenges. Finally, using the specialised capabilities of terahertz spectroscopy we can gain new insights into the physical mechanisms which underly the behaviour of surface-plasmon based electromagnetic structures.

1.2 Terahertz radiation

The term ‘Terahertz radiation’ is used to designate the under-studied gap in the electromagnetic spectrum between microwave and infrared frequencies. Along with friendlier aliases such as ‘sub-millimetre waves’ and ‘T-rays’, it refers only to the fact that the frequencies of the electromagnetic waves in this regime are conveniently expressed in multiples of $10^{12}$Hz. The range is commonly defined as lying between 0.3 and 10 THz.

A catchy name does not, in itself, make a wavelength range useful and we must have some motivation for studying materials in the terahertz range. Technologically, terahertz radiation has potential applications for non-invasive, non-ionising label-free imaging of subjects such as drugs, luggage and spacecraft. Terahertz radiation can be used to monitor processes in biochemistry, to characterise semiconductors, to analyse petrochemicals or to perform diagnostics on human breath. For more fundamental science, especially in physics, terahertz techniques can give added insight into the underlying behaviour of photonic structures and devices. By using high-energy optical frequency laser pulses, pump-probe techniques can be used to make dynamic, time-resolved alterations to the characteristics of these
At terahertz frequencies we can make subwavelength structures without resort to complex nano-fabrication techniques needed for visible radiation, and we can conveniently measure the propagation of light on the centimetre-scale. We can also make broad-band, time-domain measurements of terahertz pulses that give insight into the origins of resonances, phase-shifts and other frequency dependent effects. It is this latter, scientific set of motivations which we propose to explore in depth in this work.

1.2.1 Terahertz techniques

Sources of low-frequency radiation (microwave and radio) are generally of a different nature to sources for the optical range. At low frequencies it is possible to drive currents in radiating antennas using electronic circuits - this becomes less effective at higher frequencies due to parasitic capacitance effects. Optical sources are usually linked to the energy levels in the electronic structure of materials, such as lasing transitions and fluorescence, or to rotational/vibrational modes in molecules - however at lower frequencies these energy levels are overwhelmed by room-temperature thermal emissions. The terahertz range falls in the gap between the low-frequency and high-frequency source types, and radiation in this ‘gap’ range has been studied only relatively recently. Low-frequency sources in the radio range were built and used as early as the end of the 19th century\textsuperscript{12}, whilst experiments with visible light have been known since the Early Modern period\textsuperscript{13}. Work pushing optical sources to the far-infrared was begun at the start of the 20th Century, and these began to overlap with radio-type sources by the 1930s\textsuperscript{14}. Coherent sources of terahertz radiation\textsuperscript{15,16} were not built until the mid 1960s with the invention of the laser,
which provided the high intensity light sources required to drive inefficient optical frequency mixing processes and generate terahertz radiation.

Since the earliest experiments many other techniques for generating and detecting terahertz radiation have been developed. High intensity terahertz radiation can be generated with free-electron lasers\textsuperscript{17}, and more compact terahertz lasers have been built by scaling quantum cascade devices\textsuperscript{18}. Microwave systems have been pushed to work at shorter wavelengths using frequency multipliers\textsuperscript{19} and by adapting backward-wave oscillators\textsuperscript{20}. Using high bandwidth pulsed lasers it is possible to build a frequency-mixed source of terahertz pulses\textsuperscript{21} using nonlinear crystals, and in a related technique, charge carriers photoexcited by ultrashort pulses in a biased semiconductor antenna\textsuperscript{22} can be driven to radiate at terahertz frequencies. These latter two techniques, combined with terahertz detection methods which also use ultrafast pulses, form the basis of terahertz time-domain spectroscopy, which is discussed in detail in Chapter 2. Other techniques involving ultrashort pulses include using an ionised gas plasma\textsuperscript{23} formed by focused high-intensity pulses as a terahertz source, and using ultrashort optical pulses coupled to surface plasmons to drive nonlinear processes in metals\textsuperscript{24}. For ‘desk-scale’ experiments, it has even been shown that peeling adhesive tape can generate terahertz radiation\textsuperscript{25}.

1.3 Surface Plasmons

The second key word in the title of this thesis is plasmonic, referring to surface plasmons. These are a form of electromagnetic radiation coupled to free charges on the interface between a dielectric medium and a conductor, forming a ‘crossbreed’ mode of electromagnetic radiation - part propagating light, part charge-density os-
Chapter 1: Introduction 1.3 Surface Plasmons

cillation. We shall consider the nature of surface plasmons in terms of their field distributions and wavevectors in more detail later; however one essential characteristic is that the electric field of a surface plasmon is maximal at the interface along which it propagates, and decays away from the interface exponentially in to both the conducting and dielectric media. The localisation and confinement of the field is dependent on the material properties of the conductor and the dielectric layers by which it is bound, and this field profile can be further altered through the imposition of structure on the interface. In the optical range, the field confinement of a SP on a metal surface can be considerably less than the wavelength of light in free space at the same frequency.

Surface plasmons are exploited in numerous applications. At optical frequencies, the localised electromagnetic field of surface plasmons lends itself to high sensitivity chemical detection with very small amounts of material - such as in surface plasmon resonance sensors, surface-enhanced Raman spectroscopy, nano-plasmonic detectors and other systems. Confinement of light to an interface has potential for nanometre-scale optical guiding such as that required for photonic circuitry. These applications are given more detailed consideration in section 1.4.

1.3.1 Surface plasmon properties

The $x$-direction wavevector ($k_{sp}$) of the surface mode propagating along an untextured, optically thick conducting sheet is given by\textsuperscript{26}

$$k_{sp} = k_0 \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}},$$  \hspace{1cm} (1.1)
in which the wavevector is determined by the permittivity of the conductor ($\varepsilon_m$) and of the dielectric layer ($\varepsilon_d$) above it. $k_0$ is the wavevector in free space, $\omega/c$. Notably, from this equation we can see that if we have a material with complex dielectric functions (such as metals), $k_{sp}$ will in turn be complex. Additionally, the magnitude of $k_{sp}$ will be greater than the free-space wavevector $k_0$. This means that the surface mode must have a purely imaginary surface normal wavevector ($k_z$) to meet the momentum conservation condition

$$\varepsilon_d k_0^2 = k_{sp}^2 + k_z^2 \quad \text{(1.2)}$$

Fig. 1.1 shows a schematic of the SP (wavevector $k_{sp}$) propagating along a surface, and the evanescently decaying electric field of the surface mode in to both the conductor and the dielectric. We can write equations for the spatial extent of these decaying fields as well the propagation length of the plasmon along the surface. The decay length of the SP electric field in to the dielectric in the (normal to the surface),
$L_{sp}$ is given by the inverse of the purely evanescent surface normal wavevector $k_z$.

$$k_z = \sqrt{\varepsilon_d k_0^2 - k_{sp}^2}$$  \hspace{1cm} (1.3a)$$

$$L_{sp} = \frac{1}{|k_z|}$$  \hspace{1cm} (1.3b)$$

$$L_{sp} = \frac{\lambda}{2\pi} \left| \frac{\varepsilon_m + \varepsilon_d}{\varepsilon_m + \varepsilon_d - \varepsilon_m \varepsilon_d} \right|^\frac{1}{2}$$  \hspace{1cm} (1.3c)$$

The propagation distance of the mode along the surface in the $x$ direction, $\delta_{sp}$ is determined by the imaginary component of the $x$-direction wavevector $k_{sp}$:

$$\delta_{sp} = \frac{1}{2\Im(k_{sp})}$$  \hspace{1cm} (1.4)$$

in which $k_{sp}$ is a function of the metal and dielectric permittivities as in Eqn. 1.1.

### 1.3.2 The Drude model

In order to determine how the wave-vector, evanescent field decay and propagation length of the surface plasmon change through the electromagnetic spectrum, we must know the permittivities of the dielectric and conductor. For a planar, untextured conductor-vacuum interface the only factor in determining the SP dispersion is the permittivity of the conductor, which is always highly frequency dependent. The dielectric function of the conductor essentially determines the complete dispersion relation of the surface plasmon, and the spatial extent of the surface plasmon fields at each frequency.

The dielectric function ($\varepsilon(\omega)$) of many conductors including semiconductors and
metals can be approximated using the Drude model,

\[ \varepsilon(\omega) = \varepsilon_{\text{lattice}} - \frac{\omega_p^2}{\omega^2 + i\omega\gamma}, \]  

(1.5)

which is dependent on the scattering rate \( \gamma \) and the bulk plasma frequency \( \omega_p \); the permittivity of the lattice is \( \varepsilon_{\text{lattice}} \). For frequencies below the phonon energies in crystalline materials (which typically lie in the region 5-50 THz) this component is approximately constant and equal to the material permittivity at zero frequency\(^{27} \). Drude parameters for gold are given by Palik\(^1 \) and others\(^{28} \), and are considered in more detail in Section 1.3.4. The parameters indicate that in the visible/infrared part of the spectrum the permittivity of gold is dominated by the real component to the dielectric function, changing from \( \varepsilon_m = -1 \) to \(-500\). At frequencies below 100 THz, (the far-infrared), the imaginary component of the metal permittivity becomes predominant. The Drude model does not account for other frequency-dependent effects such as the interband transitions which give gold its distinctive colour\(^{29} \). However the Drude model is sufficient to explain the general trend in the permittivity of gold with varying frequency\(^1 \).

### 1.3.3 Surface plasmon dispersion

Now that we have a model for the frequency dependent properties of the conductor, we can plot the wave-vector, field profile and propagation length of the surface plasmon at frequencies from the microwave range (10 GHz) to the UV (1 PHz) This is shown in Fig. 1.2, in which Drude parameters for gold from Ref.\(^{30} \) are used as the dielectric function of the conductor. The wavevector (Fig. 1.2(a)) is calculated as in Eqn. 1.1. The propagation length calculated using Eqn. 1.4 (Fig 1.2(b)) is scaled
by the freespace wavelength, $\delta_{sp}/\lambda$. Similarly the extent of the electric field in the
$z$-direction from Eqn. 1.3 is normalised by the free space wavelength as $(\lambda - L_{sp})/\lambda$
to yield the normalised field confinement plotted in Fig. 1.2(c).

In Fig. 1.2(a) at 0.6 PHz there is an asymptote in the surface plasmon wavevector. This corresponds to the frequency at which the permittivity of the gold $\varepsilon_m$
is equal to $-1$; this is referred to as the surface plasma frequency labeled as $\omega_{sp}$. At frequencies above $\omega_{sp}$ the surface plasmon no longer propagates. Note also on
Fig. 1.2(a) that near $\omega_{sp}$ the imaginary component of $k_{sp}$ becomes very large. This
means that the propagation length (Fig. 1.2(b)) is greatly reduced. Just below the
surface plasma frequency at 0.55 PHz the surface plasmon propagates for less than
one wavelength. However, this region of the spectrum also corresponds to the point
at which the field confinement is maximal, as shown in Fig. 1.2(c).

Moving down in frequency towards the infrared region of the spectrum the trend
is one of increasing propagation length but decreasing field confinement with lowering frequency. Midway through the infrared (0.27 PHz) the threshold is reached
at which the spatial extent of the SP fields is actually greater than the free space
wavelength, and the normalised field confinement in Fig. 1.2(c) falls below zero.
At this point the surface plasmon wavevector is very close to the lightline, and the
mode behaves much like a photon traveling at grazing incidence along the surface.

Evaluating the SP dispersion relation at the low-frequency end of the electromagnetic spectrum, in the THz and GHz frequency ranges, the confinement is such
that the decay length of the surface mode is now much longer than the wavelength
of the incident light. The study of these loosely bound surface modes is actually
older than that of surface plasmons, with the recognition of radio waves coupled to a
conducting surface being made by Zenneck as early as 1907 (lending them the name
Figure 1.2: Frequency-dependent properties of a surface plasmon on a gold-air interface: (a) In-plane wavevector $k_{sp}$, (b) Normalised propagation length $\delta_{sp}/\lambda$ (c) Normalised field confinement $(\lambda - L_{sp})/\lambda$. In the plots $\omega_{sp}$ is indicated by a dashed line.
'Zenneck waves'). Despite not being confined to an interface, Zenneck waves still require a conducting surface in order to propagate; this constraint makes them useful in long-range radio detection and signalling, including the transmission of radio waves long distances over the curvature of the earth by following the conducting surface of the sea. At these very low frequencies the imaginary component to the dielectric function of metals actually dominates over the real part; for this reason the characteristics of the surface waves are slightly different - although still coupled to charge-density oscillations, a Zenneck wave can actually have higher phase-velocity than light in free space.

1.3.4 Semiconductor surface plasmons

We have seen above that in the terahertz range between the microwave and infra-red, planar metals do not support confined surface plasmons. The spatial extent of the fields of a surface plasmon on gold at 1.0 THz is of order 2.0 cm, compared to a free-space wavelength of 300 μm. However, in this range we have the option of using materials other than metals to support surface plasmons - in particular semiconductors.

The conductivity of semiconductors (and indeed all conductors) is determined by the number of charge carriers in the conduction band and by the mobility of those charge carriers. In a metal, with completely-filled valence bands and a part-filled conduction band, the charge carrier concentration is essentially fixed as there are no valence states for the carriers in the conduction band to occupy. By contrast, in a semiconductor there are some unfilled electron energy states in the valence bands as well as in the conduction band; this means that electrons can be transferred between
the two bands, altering the concentration of conduction electrons\textsuperscript{34}. This alteration can be made in many ways, for example by doping the semiconductor with charge donors/acceptors, by changing the temperature, by photo-exciting carriers from the valence band or by applying an electric field to form regions of charge depletion. Changing the charge carrier concentration will change the frequency-dependent conductivity of a semiconductor - this in turn will change its electromagnetic properties such as reflectivity, absorption etc. It will also change the properties of any surface modes supported by the semiconductor, and it is for this reason that it is particularly interesting to study surface plasmons on semiconductors - by changing the material properties of a semiconductor one can ‘tune’ surface modes, and importantly for the work in this thesis, correctly chosen semiconductors can support confined surface plasmons in the terahertz frequency range, as we show below.

In the Drude model of Eqn. 1.5 the bulk plasma frequency $\omega_p$ of a conductor is determined directly by the charge density $N$ and the carrier mass $m^*$; it can be written as

$$\omega_p^2 = \frac{Ne^2}{\varepsilon_0 m^*}. \quad (1.6)$$

The electron densities in metals give plasma frequencies in the UV (for example, gold has a plasma frequency\textsuperscript{35} at around 2000 THz in the near-UV, from a charge carrier density of $6 \times 10^{28}$ m\textsuperscript{-1}). In Drude-like conductors the bulk plasma frequency ($\varepsilon = 0$) and the surface plasma frequency ($\varepsilon = -1$) are relatively nearby to each other; from this we can infer that metals such as gold will support confined surface plasmons in the optical frequency range as we mentioned in Section 1.3.1. However if we take a typical\textsuperscript{34} doped-semiconductor charge density of around $10^{22}$ m\textsuperscript{-1} we find a bulk plasma frequency around 10 THz, at the top of the terahertz range -
from which we can infer that semiconductors will support confined surface plasmons in the terahertz frequency range.

As well as the plasma frequency we are also concerned with the charge carrier mobility in the conductor; in the Drude model (Eqn. 1.5) this determines the scattering rate \( \gamma \). As a general rule, the higher the carrier mobility the lower the scattering rate; electron scattering is a loss-mechanism for surface plasmons\textsuperscript{26} and so the lower the scattering frequency the longer the propagation distance for the plasmon. Gold and silver are the metals with the lowest scattering frequencies and are widely used for optical plasmonics; for their semiconducting equivalent we look to the intrinsically semiconducting \( III - V \) crystals. The ‘world-record’ in charge carrier mobility for a bulk semiconductor\textsuperscript{36} is held by the \( III - V \) semiconductor Indium Antimonide (InSb). In Fig. 1.3 we compare the dielectric function of InSb

Figure 1.3: Complex dielectric function of (a) gold in the optical range and (b) InSb in the terahertz range. Both are taken from Palik\textsuperscript{1}, with the gold being data from empirical measurements and the InSb data being from an estimate of the Drude parameters.
in the terahertz range to that of gold in the optical range. It is clear from the plots that the dielectric functions are very similar indeed, with comparable ratios between the real and imaginary parts of $\varepsilon$. From this we can infer that InSb should support an interfacially confined surface plasmon in the terahertz frequency range just as gold does in the optical range. The surface plasma frequency of InSb lies at around 1.7 THz, which is in the section of the terahertz range that is readily accessible by terahertz time-domain spectroscopy (see Chapter 2). This makes it ideally suited for experiments on highly confined terahertz surface plasmons.

1.3.5 Surface plasmon techniques

As well as an appropriate material for terahertz plasmonics we must also find a suitable experimental method for coupling radiation from free space to a surface plasmon, in particular looking at those which are suitable for terahertz wavelengths.

The primary concern in developing techniques for generating and detecting surface plasmons is to overcome the mismatch between the surface plasmon wavevector and the wavevector of light incident from a dielectric - this can be seen in Fig. 1.2(a) in which the momentum mismatch corresponds to the gap between the wavevectors on the lightline and $k_{sp}$ on the dispersion diagram. This gap can be ‘bridged’ by a number of techniques, most of which were originally developed to be used in the optical wavelength range.

Prism coupling

Reflection of light at the interface between two dielectrics (such as the total internal reflection of a beam in a prism) generates an evanescently decaying field on the low-
index side of the dielectric. This evanescent field has no real wave-vector component normal to the surface, and so can be used to couple free-space light to a surface plasmon. This can be achieved through placing a conductor in close proximity to the evanescent field from the prism, or even by coating the prism itself with an optically thin layer of the conductor\textsuperscript{37}. In experiments light is reflected from the metal film (through the prism) and reflected intensity is monitored as a function of angle or wavelength. The condition of optimum coupling to the SP corresponds to a dip in the intensity of reflected light. This technique allows direct access to the conducting surface from a probe beam, and has high sensitivity to the local environment of the metal surface - for this reason it has applications in the detection of very small changes in refractive index and in surface spectroscopy\textsuperscript{38}.

**Figure 1.4:** (a) Prism coupling to a surface plasmon (b) Grating coupling. (c) Coupled surface plasmons in a waveguide.
Coupling with surface structure

A periodic structure on a surface, such as a sinusoidal grating, can scatter incident light through Bragg reflections$^{39}$. This scattering extends the region in momentum space in which the incident light is able to couple to modes. The grating has a period $\lambda_g$ which leads to a grating wavenumber $k_g$; the scattering event can add momentum to the free-space light$^{40}$ such that $k_{\text{scattered}} = k_{\text{light}} + nk_g$ where $n$ is an integer number of grating vectors. By finding the matching condition such that $k_{\text{scattered}} = k_{\text{sp}}$, light can be coupled to a surface plasmon. Using this method it is possible to achieve nearly complete coupling of the incident light to a SP$^{41}$. Similarly to the technique used for prism coupling, SP resonance is usually determined by a reduction in the specular reflectivity of the grating when the light is at the optimum wavelength and angle for SP coupling. This excitation process allows direct illumination of the surface and changing the parameters of the grating affords a degree of control over the mode propagation$^{40}$ and surface plasmon resonance frequency.

Another method of coupling to a surface plasmon by structuring a surface is to roughen the conducting layer; this gives broadband, multi-directional coupling to a surface plasmon$^{26}$. Roughened surfaces are used for surface-enhanced Raman spectroscopy measurements$^{42}$. However, in these measurements the roughened surface also compromises the propagation of the surface plasmon.

Scattering centres

A generally less efficient, yet highly flexible method of coupling radiation to a surface plasmon mode is to scatter the incoming light at a single centre. A point, edge or aperture can scatter the wavevector of incident light in many directions, in con-
trast to the highly directional scattering of a grating. Some of the light scattered by a point will match the surface plasmon wave-vector \( k_{SP} \), and couple to a mode propagating along the surface. This method is relatively inefficient (compared to the almost 100% coupling which can be achieved using a grating or a prism), however it does allow broadband surface plasmon coupling and can be convenient for propagation experiments.

A particular scattering technique used in this thesis is the placement of sharp apertures directly above a conducting surface to couple incident light into radiation. In Fig. 1.5 we show a focused beam of light illuminating an aperture which scatters some of the light into a surface plasmon propagating along the conducting layer. After propagating some distance, the surface plasmon is coupled back into free-space radiation with second scattering aperture. This geometry ensures that any light not propagating parallel to the conducting surface will not reach the detector. Such a geometry is described for experiments in infrared surface plasmons by Agranovich\(^43\), and has been used more recently for terahertz experiments on semiconductors\(^44\). In contrast to the optical techniques of prism or grating coupling, it does not rely on monitoring a decrease in the intensity of the reflected incident light beam at the point of SP resonance, but rather on direct detection of light which has propagated as a surface plasmon. The broadband scattering of the apertures allows us to excite and detect the surface plasmon at multiple frequencies simultaneously, and so is well suited to broadband pulsed terahertz measurements. The length-scales involved in this experimental geometry are such that it is generally unsuitable for high-frequency measurements - the gap between the blade edge and the surface must be wavelength-sized, and the distance between the blades must be less than the propagation length of the surface plasmon which is typically microns in the optical range. However,
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1.4 Surface plasmon applications

at lower frequencies (infrared and below) these constraints become less problematic and the technique becomes practical for experimental measurements.

1.4 Surface plasmon applications

As mentioned briefly in Section 1.3, one of the prime motivations behind surface plasmon research is the potential for technological applications, which cover diverse areas including optical interconnection, spectroscopy and wave-guiding.

1.4.1 Subwavelength light guiding

Surface plasmon based interconnects have been proposed as a way of guiding light in optical circuitry and other devices; the subwavelength confinement of surface plasmons allows one to reduce the size of the interconnect to much smaller diameters than that of an optical fibre. However, this confinement is usually at the expense of increased attenuation over distance. Recent progress in the field of plasmonic interconnect development has included the demonstration of surface plasmon guiding around curves and corners, and of reducing the polarisation dependence inherent
in surface plasmon devices which is problematic for telecoms systems. At terahertz frequencies there is a considerable amount of literature on using metal wires as a plasmonic waveguide - although they do not support confined plasmons, wire guides make convenient ‘endoscope’ systems and focusing devices for terahertz light.

1.4.2 Spectroscopy

A primary application which will be explored somewhat in this thesis is the use of surface plasmons for material spectroscopy. It is desirable in many systems to detect extremely small amounts of material, such as in a low-yield biological or chemical experiment. Optical spectroscopy can detect changes in absorption spectra rapidly and without perturbing the sample through the use of probes or chemical interaction. However, relatively large samples are required for visible-wavelength light spectroscopy in order to have sufficient interaction between the light and the sample for reliable detection. When measuring at terahertz wavelengths this constraint becomes even more pressing - many biological systems simply cannot produce the centimetre-scale volumes of material required for terahertz spectroscopy.

Confined to the interface of a surface, the field of a surface plasmon can interact with a thin film of material in the range of the evanescent decay of the surface plasmon electric field, \( L_{SP} \), which can be considerably less than the wavelength of light (section 1.3.1). If a sample can be prepared in to a film or liquid layer next to a conducting surface, very small amounts of the material can be analysed using a surface plasmon coupled to the conductor. At optical frequencies, these measurements are of sufficient sensitivity to detect absorption of gas in to an organic layer or binding events on antibodies placed on the surface; at terahertz frequencies
surface spectroscopy on metal guides has been used to monitor chemical processes in DNA\(^7\). In chapter 4 we explore this application by showing that the confined field of a terahertz semiconductor plasmon can be used to detect subwavelength films of a dielectric analyte.

1.5 Surface modes in structures

As well as being interesting to study in their own right, surface plasmons can be found as part of transmission pathways in more complex structures. Two such structures are considered in this work - a single subwavelength slit in which surface modes mediate transmission through a resonant cavity is studied in Chapter 3, and in Chapter 5 experiments are performed on an array of subwavelength holes which exhibit high levels of transmission due to constructive interference from a surface-mode transmission pathway in the structure.

In these structures surface plasmons are found in non-uniform geometries; these can perturb the surface plasmon wave-vector significantly from that described for a planar interface in section 1.3.1. Previous studies have shown the properties of surface plasmons in metal-insulator-metal slab waveguides\(^55,56\) (see Fig. 1.4(c)) and numerous more exotic geometries such as square-sided guides\(^47\), hybrid surface/wire geometries\(^57\) and plasmonic photonic crystals\(^58\).

1.5.1 Subwavelength slits

In 1999 it was shown by Porto et. al\(^59\) that subwavelength slits in a metal film could exhibit very high levels of transmission at optical frequencies. Although a slit is arguably the simpler structure, this work was subsequent to studies showing
enhanced transmission through arrays of holes by Ebbesen et al.\textsuperscript{60}. The mechanism underlying the transmission enhancement in both slits and holes has been the subject of considerable debate, especially as to the precise role which surface modes play in enhancing transmission levels\textsuperscript{61–65}.

The transmission enhancements seen in slit systems are generally brought about by two aspects of the structure\textsuperscript{66} - either by resonances arising from the length of the slits themselves, or by the periodicity of a slit array. The effects of slit-length resonances can be seen in both isolated single slits and in arrays, whereas an array is a prerequisite for resonances arising from periodicity. It is the former, isolated single-slit system which is considered in detail in Chapter 3 of this thesis, in which we take a slit formed in InSb and use terahertz time-domain spectroscopy to find the factors determining resonance position and amplitude. We show the interplay between the effects of changing the slit width and the changing permittivity of the conductor.

\textbf{Figure 1.6:} Surface plasmons on the top and bottom interfaces of a sub-wavelength slit
in determining the resonance characteristics, and the phase information from the
time-domain terahertz measurements allows us to measure the effective index for
the radiation propagating through the slit. Phase-resolved measurements are an
important feature of terahertz time-domain spectroscopy, and they are discussed in
detail in section 2.7.

We show that the transmission of light through the InSb slits is enabled by
surface plasmons on the top and bottom interfaces of the slit (Fig. 1.6). These
form the well studied metal-insulator-metal surface plasmon geometry\textsuperscript{55}, in which
the surface plasmon propagation depends on both the material properties of the
conductor and the width of the slit. For narrow slits, in which the fields of the two
opposing surface plasmons can interact, the propagation changes considerably from
that of a surface plasmon on a planar interface. In this system there is an index
mismatch between the surface plasmon modes inside the slits and the free space
modes in the air beyond the conducting screen. This causes reflections at the slit
entrance and exit, which leads to Fabry-Pérot-like cavity modes along the length of
the slit and corresponding resonance maxima in the transmission spectrum of the
slit.

\subsection*{1.5.2 Arrays of subwavelength holes}

An individual isolated subwavelength hole (with sides of length $a$) in a conducting
screen will transmit a very limited amount of radiation\textsuperscript{67}, which scales with $(a/\lambda)^4$.
In 1998 it was shown by the seminal work of Ebbesen et. al.\textsuperscript{60} that by taking such
holes and forming them in to an array, the transmission level can be enhanced by
many orders of magnitude above that expected from the $(a/\lambda)^4$-dependent trans-
mission level. The precise mechanism underlying this enhancement has been the subject of some debate. However in many cases it can be attributed to the coupling of incident light to surface plasmons on the conducting interface in which the holes are formed (see Fig. 1.7). A surface plasmon supported on the metal surface containing the holes gives the radiation a ‘second chance’ to transmit through the holes - effectively increasing the level of interaction of the light with the holes. This effect has been shown for terahertz radiation\textsuperscript{68}, microwaves\textsuperscript{69} and for visible light\textsuperscript{70,71}. This physical mechanism is distinct from the surface plasmons which mediate the transmission the subwavelength slits of Section 1.5.1; the slits support propagating surface plasmon modes \textit{inside} the slits, whilst subwavelength holes support only purely evanescent modes. The transmission-mediating surface mode is across the hole array surface, as illustrated in Fig. 1.7.

In Chapter 5 we measure terahertz transmission through arrays of subwavelength holes in a film of gold, and link the transmission properties directly to the characteristics of the surface mode mediating the transmission. This is extended in Chapter 6 in which the surface mode propagation is controlled dynamically by using pulses of visible radiation to photoexcite the surface of the structure with optical-pump,
terahertz-probe spectroscopy (section 2.10).

1.6 Finite element modelling

For simpler systems the characteristics of surface plasmons can be calculated using purely analytical formulations. It is possible to model many planar three-layer systems without even resorting to a numerical solution. Simple periodic structures can be modeled using modal-matching techniques (see Chapter 5) so long as the boundary conditions of the periodic unit cell and the interfaces can be well defined. With more complex systems (such those with asymmetry, finite dimension or hard-to-define boundary conditions within the structure) it is necessary to use computational techniques such as finite element modelling.

The strategy of finite element modeling techniques is to solve the full electromagnetic response of a structure by splitting it into a series of smaller elements - each element having a response which can be calculated from Maxwell’s equations. This discretisation requires the elements to be smaller than the wavelength of light being solved for, and can lead to substantial numbers of elements in a model. In order to limit the number of elements required to computationally feasible quantities, the discretisation is typically combined with boundary conditions (such as structural periodicity or semi-infinite boundaries). In this thesis the commercial finite element package HFSS is used.

Discretisation

The nature of the discrete elements used to approximate a structure determines to a large extent the speed and accuracy of a simulation. Some discretisation systems
use regular cubes; for a square-sided structure this has speed advantages and reduces computational complexity. However, in the case of structure with oblique or curved surfaces, the number of elements required to accurately approximate the surface becomes very large. HFSS uses irregular-sided tetrahedra; this offers enhanced reproduction of oblique and curved surfaces with fewer mesh elements.

Material parameters

The properties of materials can be defined using just the complex permittivity and permeability. This is adequate for materials with low permittivity. However, when the permittivity of a material is very high (such as in a metal or other conductor), the wavelength of any radiation inside said material becomes very small. This means that size of the mesh elements must be similarly scaled. Because metals can
have complex refractive indices with magnitude higher than $10^3$ in the terahertz range, a model directly incorporating such material parameters will rapidly become computationally infeasible. For this reason a surface conductivity approximation can be made to the material in which a single layer of tetrahedra on the surface provides an impedance equal to that of the metal interface; although this reduces computational complexity, it makes it impossible to calculate the electric fields inside the conductor, or to measure electric fields which have transmitted partially through a conductor - effectively constraining the use surface approximations to optically thick metal structures. In fact, for the low frequency range it is often adequate to treat metals as perfect electrical conductors (PEC), especially in cases where radiation has a short interaction length with the metals - this can be achieved using an infinite surface conductivity in HFSS.

**Boundary conditions**

In order to define an infinitely repeating periodic structure, Master-Slave boundary conditions can be defined. These impose the condition that the electric fields on the Master boundary are equal to those on the Slave boundary, with an associated phase-shift corresponding to the length of the unit cell. In general it is only necessary to model a single unit cell of a periodic structure, and impose Master-Slave boundaries on the repeating interfaces.

Some systems are symmetrical about one plane; for this case a ‘Perfect E’ boundary can be used. This boundary simulates a perfect electric conductor bisecting the model, and it reproduces a mirror image of the electric field from the model side of the boundary on the opposing side - essentially assuming that field is perfectly symmetrical either side of the boundary plane. This condition halves the computa-
tional requirements for a symmetrical structure. Similarly a ‘Perfect H’ boundary represents a perfect magnetic conductor and produces a mirror image of the magnetic field. The choice of E or H field boundaries depends on which of the fields is aligned tangentially to the boundary.

**Forming a model**

Structures for simulation are drawn in HFSS using a Computer Aided Design (CAD) system, assigning material properties to each element. The same CAD system is used for the assignment of boundary conditions as above, shown in Fig. 1.8. Forming a mesh of tetrahedra is automated, with the mesh refinement algorithm concentrating extra tetrahedra in regions of higher field. Additionally, manual mesh adjustments (constraints on the size and number of mesh elements in a given region) can be made taking in to account known features of the system which may manifest themselves as something more complex than simply high electromagnetic fields - for example, in the surface plasmon propagation simulations of Chapter 4 we simulate the out-coupling of a surface mode which has propagated some distance; because this surface mode is highly attenuated at the point of out-coupling the automated meshing algorithm largely neglects it in the allocation of tetrahedra, concentrating instead on the high-field regions of the input coupler. Mesh operations can be used to force extra tetrahedra in to the output coupling region, providing a more accurate result for the calculated fields in the region of interest.

Once a model is solved, parameters such as the field strength in a particular region can be directly extracted. For many applications the total transmitted field amplitude through a structure is the quantity of interest, and this can be calculated by taking the average field over a 2D plane in the model.
1.6 Finite element modelling

The ability to calculate fields at any point in the model can, in some cases, make a finite element model more useful in determining the underlying physics of a structure than a purely analytical consideration. Visualisations of power flow and field intensity in the structure can provide evidence of particular transmission pathways and material interactions. However a finite element model generally lacks the facility to split the behaviour of a structure into discrete mathematical quantities as can be achieved with some analytical methods. Finite element modelling is also compromised in the speed of calculation when compared to analytical formulations; large models can take several hours to solve.
Chapter 2

Terahertz time-domain spectroscopy

Summary

This chapter describes the experimental methods used for terahertz time-domain spectroscopy, including details of the laser systems, terahertz generation and terahertz detection methods used. Consideration is given to various noise-reduction schemes. Finally we consider optical-pump, terahertz-probe measurements.

2.1 Resolving phase

Resolving the full electric field profile of electromagnetic radiation is often experimentally challenging and has driven the development of some of the more sophisticated techniques of optics; the information that can be gleaned from phase measurements can be highly valuable - for example, the famous experiment of Michelson and Morley, demonstrating the constancy of the speed of light and non-existence of the ether, was founded on an interferometer sensitive to the phase of radiation.

Phase resolution of monochromatic sources with interferometry is well developed, but with broadband pulsed radiation interferometry techniques are less use-
ful. The complex, rapidly-changing field profiles of broadband pulses can contain a great deal of information which is not readily accessible. Modern developments in phase-sensitive pulsed optical experiments have included phase-resolved near field techniques\textsuperscript{74} such as Scanning Near-field Optical Microscopy (SNOM), and ultra-short pulse based systems such as Frequency Resolved Optical Gating (FROG) and associated variants\textsuperscript{75}. For lower frequencies, Microwave systems are readily phase-resolved using fast electronics\textsuperscript{76} in vector-network analysis systems. In between these two ranges (the infrared and the microwave) there is a gap in the availability of radiation sources and detectors, for both phase-resolved measurements and more conventional intensity measurements. This gap essentially originates from the energy levels found in nature - optical systems such as lasers are driven by energy transitions which must be maintained in population inversion. Maintenance of population inversion in those few systems which do have low-frequency (sub-infrared) electronic energy gaps is confounded by thermal effects at room temperature. Microwave systems are driven by electrical currents which are compromised by parasitic capacitance at higher frequencies. The result is that between 100 GHz and 10 THz there is a scarcity of techniques for generating and measuring electromagnetic radiation. The few effective terahertz sources which do exist have only recently reached sufficient maturity to be found outside the laboratory.

2.1.1 Terahertz sources

There are two fundamental approaches to filling the terahertz ‘gap’ in radiation sources - either scaling the techniques used for microwave systems, or adapting optical and infrared techniques to generate radiation at lower frequencies. An example
of the latter approach is scaling the designs of quantum cascade lasers\textsuperscript{18}; these are efficient, solid-state CW sources which typically work in the infrared range. Current designs for terahertz quantum cascade lasers typically require cryogenic environments in which to operate; much progress has been made in recent years in adapting these lasers to work at lower frequencies, higher powers and higher temperatures. However, short of regular interferometric techniques, quantum cascade sources are not suitable for phase-resolved measurements due to their CW nature and the difficulty of synchronising the emission with a high-speed detection system. Other common ‘optical’ type terahertz sources include frequency mixed CO\textsubscript{2} lasers\textsuperscript{77} and pulsed free electron laser sources\textsuperscript{17}, both of which produce narrowband, continuous-wave beams of terahertz radiation.

The approach of adapting microwave technology generally involves scaling Schottky diodes\textsuperscript{19} to work at higher frequencies than the GHz range. This is difficult, as parasitic capacitance reduces emission levels of high frequency microwave systems drastically - however, these sources have the advantage that they can be directly connected to electronic systems, and would be relatively cheap to produce in large quantities. Although it is possible to generate radiation near the terahertz range from a frequency-multiplied microwave source, resolving the phase of the radiation is impossible using fast electronics - ultimately the detection electronics must be able to operate as quickly as the rate at which the electric field of the radiation under detection changes. This limits the maximum working frequency for a vector network analyser to below 100 GHz. Backward wave oscillator microwave sources are similarly constrained by parasitic capacitances.

Terahertz time-domain spectroscopy (THz-TDS) is a phase-resolved, room temperature technique which can be carried out using commodity optical hardware.
THz-TDS is especially accessible with modern improvements in the usability and affordability of Ti:Sapphire ultrafast laser systems. It is this latter system which will be described in detail in this chapter with emphasis placed on the design of spectrometer used in the experiments in this thesis.

2.2 THz-TDS Overview

In terahertz time-domain spectroscopy techniques the generation and detection of terahertz pulses is coupled to a source of optical-range ultrashort laser pulses; typically from a modelocked Ti:sapphire laser. There are two prevalent source/detector systems, one based on the generation of terahertz pulses in non-linear crystals and the other on emission of terahertz radiation from semiconductor dipole antennas. In both of these systems ultrashort infrared pulses illuminate the emitter; terahertz pulses from the emitter are then collimated and directed on to the sample or system under investigation in the spectrometer. After interacting with the sample the terahertz radiation is collected for detection, which is perhaps the most interesting aspect of the system. Transmitted terahertz pulses are focused on to the detector simultaneously and colinearly with pulses of an optical probe beam, taken from the same laser used to drive the terahertz emitter. Changes to the polarisation state of the optical probe pulses after they propagate through the detector allow us to monitor the applied terahertz electric field. Most importantly, because the probe pulses are typically of just 0.1 ps duration and are in synchronisation with the terahertz pulses, it is possible to measure the electric field of the terahertz pulse as a function of time. Terahertz pulses have cycle durations of around a picosecond, meaning multiple samples of the steepest pulse features can be made with sub-picosecond
ultra-short pulse.

2.3 Time-domain spectra

Before moving in-depth to the details of the experimental techniques for generation, detection and optimisation of time-domain terahertz spectra we shall look at the end result. In Fig. 2.1(a) we show an example of a terahertz pulse transient measured using the spectrometer described in more detail below. The full electric field as a function of time \( E(t) \) is plotted, with a resolution of 0.05 picoseconds per point. The pulse is essentially a single cycle of radiation, with a small amount of ‘ringing’ oscillation trailing the main pulse. The random amplitude variation of each electric field point (i.e. the background shot-noise level) is approximately \( 1/10,000^{th} \) of the peak electric field amplitude. The acquisition time for the trace shown is approximately two minutes. Taking the Fourier transform of the terahertz pulse yields a frequency-domain spectrum, \( E(\omega) \), as shown in Fig. 2.1(b). As well as the amplitude of each frequency component within the pulse we also extract the accompanying phase as a function of frequency, \( \phi(\omega) \).

2.4 Laser sources

The starting point of our terahertz time-domain spectroscopy system is the amplified pulsed laser source used to drive the experiments. We use a Ti:Sapphire system consisting of two laser cavities - a seed and an amplifier. Titanium-doped sapphire crystals exhibit optical gain and stimulated emission over an exceptionally broad wavelength range, from 650nm to 1.1 \( \mu \)m. This broadband lasing response gives the
Figure 2.1: (a) An example of a time-domain measurement of a terahertz electric field transient. (b) Frequency-domain plot of the above pulse, showing both the electric field amplitude and phase.

Chapter 2: Terahertz time-domain spectroscopy

2.4 Laser sources
lasers a high tuning range, but more importantly for our application it allows for the generation of high bandwidth, short-duration pulses. In the seed system used for all the experiments in this thesis (Coherent Vitesse), the gain medium is pumped using a green-wavelength (535nm) diode laser, with the IR pulses generated having a centre bandwidth of 800nm and a duration of 85 femtoseconds; pulse energy is approximately 12 nJ at a repetition rate of 80 MHz.

As we shall detail later, for nonlinear optical experiments (such as terahertz time-domain spectroscopy) there is great benefit to be gained through increasing the laser intensity to drive $\chi^{(2)}$ processes. For this reason we add a regenerative amplifier (Coherent Legend Elite) to produce higher energy pulses, albeit at a lower repetition rate. The regenerative amplifier is essentially a second Ti:Sapphire laser cavity (in this case with its own diode pump laser) optically isolated from the oscillating seed laser. Before entering the amplification cavity, the seed pulses are temporally stretched using a reflection grating and re-collimating optics. Individual stretched seed pulses are switched in to the Legend cavity using a Pockel’s cell, and are amplified in the cavity over the course of approximately 20 round-trips. The stretching process minimises the high instantaneous intensity that would be found in the amplifying cavity for sub-100fs pulses, avoiding damage to the gain media. Once amplified, the pulse is switched out of the cavity by a second Pockel’s cell, and is re-compressed in to a 100 femtosecond pulse using another grating - reversing the stretching stage. The output of the amplifier is a chain of 3.0 mJ, 100 fs pulses at a repetition rate of 1.050 kHz. Although the repetition rate has been lowered by a factor of $8 \times 10^4$ from the seed pulse rate (necessitating an increase in the acquisition time for measurements), the instantaneous pulse intensity has been raised by a factor of $2 \times 10^6$ - for a nonlinear experiment the accompanying quadratic increase in
Figure 2.2: Calculated response of a semiconductor dipole antenna (using calculations and data from Lee et al.\textsuperscript{2}) and of an idealised ZnTe crystal (calculations again from Lee) to varying fluence of 800nm excitation beam. The calculations are for a hypothetical lossless ZnTe crystal and do not consider differences in the terahertz pulse shape between the two emitters.

the $\chi^{(2)}$ signal will more than compensate for the reduction in the number of pulses per second arriving at the detectors.

2.5 Terahertz generation

2.5.1 Semiconductor dipole antennas

As mentioned previously, there are two main methods for the generation of terahertz pulses from NIR ultrashort pulses. The first which must be acknowledged is the technique of using a NIR pulse to form a small dipole\textsuperscript{22} between two electrodes
applying a high voltage bias to a semiconductor slab; photo-excited charge carriers in
the semiconductor short the electrodes and in doing so emit pulses with a functional
form dictated by the acceleration of the charges excited by the NIR pulse. In the case
that the NIR pulse is of short (100 fs) duration, the emitted radiation can extend in
to the terahertz range. In this source the electric field amplitude produced is linearly
proportional to the intensity of the NIR photoexcitation pulse for low intensity
excitation. For high intensity photoexcitation saturation behaviour is seen\(^2\). For
this reason it is particularly suitable to use with low pulse-energy generation beams
such as those produced by Ti:Sapphire oscillators alone. However, in the case where
higher energy pulses are available it makes sense to exploit the quadratic gains in
terahertz generation which can be attained through the use of nonlinear effects.

Fig. 2.2 shows a plot of the theoretical peak field intensity of terahertz genera-
tion versus intensity of the pump laser pulses for a biased dipole antenna\(^2\) (which
saturates at 3.0 kV/cm) and for optical rectification in a ZnTe crystal\(^2\). Because
of the saturation behaviour the peak terahertz field from a ZnTe crystal rapidly
becomes much higher than that from a dipole antenna at high pulse energies. With
un-amplified lasers (typically pulse energies being less than 2 nJ) it is difficult to
reach fluences of greater than 0.1 mJ/cm\(^2\) even with extremely tightly focused spot
sizes. For these lasers it makes sense to use a dipole antenna. In contrast, with an
amplified laser system (pulse energies around 1 mJ) it is easy to reach fluences of
more than 2 mJ/cm\(^2\) even when taking just a small fraction of the beam, at which
point the ZnTe crystal is the more efficient generation medium. The only limi-
tation on the terahertz field which can be generated through optical rectification
is the thermal damage threshold of the nonlinear media. Using very high optical
pulse energies and large-area ZnTe crystals it is possible to create extremely high
field-strength terahertz pulses\textsuperscript{78}.

### 2.5.2 Difference frequency mixing

We shall consider in more detail the use of nonlinear crystals to generate terahertz pulses through difference frequency mixing.

The full polarisation response of a material can be described by a function of its susceptibility, $\chi$. For linear systems, the polarisation of the medium $P$ can be written as\textsuperscript{79}:

$$P = \chi^{(1)} \cdot E(\omega)$$

for all frequencies.

However in nonlinear materials $\chi$ can be expanded as a series of terms each dependent on combinations of the frequency of the driving field. If we consider a simple case where there are two driving electric fields $E_1$ and $E_2$ with frequencies $\omega_1$ and $\omega_2$, the polarisation becomes:

$$P = P^{(1)} + P^{(2)} + P^{(3)} + \ldots$$

$$P^{(1)} = \chi^{(1)} \cdot E(\omega)$$

$$P^{(2)} = \chi^{(2)} : E_1(\omega_1)E_2(\omega_2)$$

$$\chi^{(2)} = \chi^{(2)}(\omega_1 + \omega_2) + \chi^{(2)}(\omega_1 - \omega_2) + \chi^{(2)}(2\omega_1) + \chi^{(2)}(2\omega_2) + \ldots$$

The introduction of the higher order terms leads to frequency conversion in the nonlinear medium. The atomic and electronic structure of the crystal in question determines the size of the $\chi^{(2)}$ coefficient; a high $\chi^{(2)}$ leads to familiar effects such as
frequency doubling. The term we are interested in is the $\chi^{(2)}(\omega_1 - \omega_2)$ component, dependent on the difference between the two frequencies propagating through the medium. The bandwidth of a 100fs pulse of 800nm radiation is approximately 15 THz, so by frequency substraction we should be able to generate a pulse containing frequencies from 15THz to near DC, given a material with an appropriate $\chi^{(2)}$ coefficient in the terahertz range.

### 2.5.3 Zinc Telluride - nonlinear effects

There are numerous crystals with a high $\chi^{(2)}$ coefficient in the terahertz range; one of the most commonly used being Zinc Telluride (ZnTe) - this is chosen as its terahertz refractive index is sufficiently close to its IR refractive index to allow for efficient phase-matching between the terahertz and generation pulses.

The upper frequency limit of the terahertz response is not limited directly by the bandwidth of the IR generation pulse, but by the absorption of the ZnTe optical phonon - the same phonon resonance produces the nonlinear response in its vicinity. For this reason bandwidth can be maximised by reducing the crystal thickness to minimise high-frequency absorption; this involves trading off against the absolute amplitude of the generated THz pulse due to the reduction of the interaction length of the IR pulse with the generation medium. The optical generation beam focused in to the nonlinear crystal is smaller than the wavelength of the terahertz pulses which are produced - the generation spot acts like a point source of radiation giving a highly divergent terahertz beam. Furthermore, the generation beam is focused and hence slightly converging in the crystal - this leads to mismatch between the wavevectors subtracted in the optical rectification process, and even greater diver-
gence in the emitted terahertz beam. To counter this divergence the terahertz beam is collimated using an off-axis parabolic mirror, see Fig. 2.3. The collimated beam can be re-focused at a sample through the addition of two extra parabolic mirrors in the middle of the terahertz path, or for sufficiently large area samples requiring minimal spread in the angle of incident radiation, samples can be placed directly in the collimated beam. After propagating through the sample pulses are focused down for detection on to an electro-optic crystal.

2.6 Electro-optic detection

It is possible to change birefringence of certain materials through the application of an external electric potential - the Pockels effect. This effect is used with high potentials in combination with polarisers for switching devices and modulators. In our terahertz detection scheme, the externally applied electric field is the terahertz pulse and the electro-optic material is a second crystal of ZnTe - the high $\chi^{(2)}$ coefficient is linked to similarly high electro-optic coefficients. ZnTe is again chosen for the good match between its refractive indices in the terahertz and NIR ranges.

We probe the electro-optically induced change in the birefringence of the ZnTe using a detection beam of 800nm pulses from the Ti:sapphire laser - split away as 1% of the THz generation beam, before it reaches the generation crystal. The detection beam is then routed, via a delay line, to the detection crystal, and propagates colinearly with the terahertz beam through the crystal. In the diagram of Fig. 2.3 the detection beam is reflected from the back interface of the ZnTe crystal - the reflected beam is near co-linear with the incoming terahertz beam. Alternatively, for larger diameter parabolic mirrors it is possible, using a small hole, to direct the
Figure 2.3: Schematic of a collimated-beam terahertz time-domain spectrometer. Red lines indicate the 800nm IR beam, blue lines a 400nm beam, orange shading the terahertz path. The dashed red line indicates an alternative route for the detection beam, through a hole in the second parabolic mirror. Black lines indicate electrical connections.
detection beam through the back of the mirror which focuses the terahertz pulses on to the detection crystal, and send them directly through the crystal colinearly with the terahertz pulses - this alternate route is shown as a dashed line in Fig. 2.3.

Owing to the birefringence of the crystal, the detection beam becomes elliptically polarised as it propagates through the zinc telluride. As the axis of birefringence is changed with the externally applied electric field, so too does the ellipticity of the detection beam; it is straightforward to detect this change through polarimetry. Shown in the lower half of Fig. 2.3 is a quarter-wave plate and splitting polariser. The quarter-wave plate converts the detection beam from elliptical to circular polarisation, the two components of which are separated by the polariser. The intensity of the two components is monitored by a differential amplifier; if the two beams are set to the same intensity, the difference in intensity between them is linearly proportional to the applied terahertz electric field.

A key aspect is the careful manipulation of the optical path length of the terahertz beam and the detection beam. The time gap between pulses from the amplified laser is around 1 ms, corresponding to a path length of 300 km; for this reason generation and detection cannot be performed by successive pulses, but must be accomplished using parts of the same original pulse from the laser. The duration of a terahertz pulse is typically around two picoseconds, whereas on a 1-meter scale optical bench the pulses propagate for several nanoseconds. Therefore in order to detect terahertz pulses the detection pulse must arrive at the detection crystal simultaneously with the terahertz pulse. This can be achieved to a large extent through careful manipulation of the optical path lengths of the two beams through choice of route across the table. Fine manipulation is by means of a motorised delay line (see Fig. 2.3) in the detection beam. Moving the motorised delay line changes
the temporal overlap between the terahertz and detection pulses; this automated control over the temporal overlap allows us to scan the arrival time of the detection pulse under computer control. Because the 0.1 ps ultrafast detection pulse is so much shorter than the two-picosecond terahertz pulse, by changing the delay of the detection pulse it is possible to map out the electric field of the terahertz pulse as a function of time. The ultrashort pulse is effectively a probe of the instantaneous terahertz field; the temporal resolution such that it is possible to take multiple samples of the field within the picosecond cycle-time of the terahertz pulse. The result of these samples is the time-domain trace of Fig. 2.1(a) which was described in section 2.3.

2.6.1 Crystal orientation

As the ZnTe is birefringent the detection efficiency is not independent of crystal orientation; the work of Planken et al. shows that detection efficiency varies sinusoidally with crystal rotation. Furthermore, there is a limited set of crystal rotation positions for which the response at the detectors is linearly proportional to the applied terahertz electric field (see section 2.6.2). Similarly, the orientation of the generation crystal and polarisation of the generation beam determine both the amplitude and polarisation of the generated terahertz radiation. This gives a set of free parameters - polarisation of the NIR generation beam, NIR detection beam and terahertz radiation and their relative intensities, which are all co-dependent with crystal orientation. Optimising for maximum terahertz signal is therefore an iterative process, maximising the generated signal through rotating the crystals and the NIR polarisation optics. After optimisation the spectrometer must be tested to
ensure that response of the detector to terahertz electric field is linear.

2.6.2 Linearity

We stated above that the intensity change at the photodiodes was linearly proportional to the applied terahertz electric field. This is not strictly accurate as the intensity changes sinusoidally with the change in the probe beam polarisation\(^80\). However, provided that the polarisation rotation \((\phi)\) is small, we can make the small-angle approximation for small values of \(\phi\) that \(\sin(\phi) = \phi\). Linearity of the spectrometer can be tested by performing the same measurement using two different strengths of terahertz electric field - for example, measuring normalised transmission through a silicon wafer with two different intensities of terahertz generation beam; if the electric field measurement is still linear the normalised transmission will be independent of the terahertz field strength.

2.7 Analysis

2.7.1 Frequency domain spectra

The samples of terahertz electric field taken using the experimental method of section 2.6 produce traces of the type shown earlier in Fig. 2.1(a). The trace is not a single continuous function, but a series of discrete data points \(E_n(t)\) for which we must use the discrete fourier transform, defined as

\[
E_n(\omega, \phi) = \sum_n E_n(t) e^{-im\omega t}
\]  

(2.3)
in which $n$ is the number of points in the input time-domain trace, and $m$ is the number of discrete points in the resulting frequency domain spectrum. This numerical calculation can be performed rapidly and easily using the Fast Fourier Transform algorithm. The Fourier transform yields the complex electric field, including both the phase ($\phi$) and amplitude of each frequency component $E_n(\omega, \phi) = E_a(\omega)e^{i\phi(\omega)}$

### 2.7.2 Normalisation

In order to eliminate the frequency response of the instrument, most transmission measurements require normalisation. We can measure two electric field traces, $E_{\text{ref}}(\omega, \phi)$ (in free space) and $E_{\text{sample}}(\omega, \phi)$ (through the sample) and normalise them to find the amplitude transmission coefficient of the sample, $t$:

$$t = E_{\text{sample}}(\omega, \phi)/E_{\text{ref}}(\omega, \phi) \quad (2.4)$$

Because our frequency domain spectra are complex, this normalisation yields both the amplitude change and the phase-shift ($\Delta \phi$) across the sample; from this information it is straightforward to extract the full complex dielectric function of a sample from a single measurement using the Fresnel equations$^{82}$. A key assumption in this normalisation is that the initial time domain trace extends for a sufficient duration that all of the features of the transmission are recorded. In samples exhibiting a narrow transmission resonance the electric field of the transmitted radiation can extend to much longer duration than the initial terahertz pulse which excited them. Similarly, samples may exhibit multiple reflections which lead to a train of terahertz pulses following the initial transmitted pulse. Fundamentally the time-domain scan-length $\Delta t$ determines the frequency resolution by $\Delta \omega = 2\pi/\Delta t$, which imposes a
lower limit on the narrowest frequency-domain feature which can be resolved for a given scan length.

2.7.3 Noise analysis

In the time-domain traces, shot-noise produces uncertainty in the terahertz electric field amplitude and a variation in the ‘zero level’ of the pulse - an example of shot noise in a time-domain trace is shown as Fig. 2.4(a) A useful metric to judge the noise level of a particular trace is to compare the size of the background noise level (i.e. the average magnitude of the signal at a time point away from the terahertz pulse) to the peak terahertz electric field. Using this metric it is possible to reach signal:noise ratios of over 5,000:1 with appropriate detection electronics.

The time-domain noise transforms to a typical $1/\omega$ noise spectrum in the fre-
Reducing noise

The efficiency of terahertz generation and detection described above is low; the terahertz pulses are sub-nanoJoule energy and the electro-optic effect from their 1kV/m field at the detection spot corresponds to very small changes in the polarisation of the probe pulse. Simply monitoring the intensity of the signal on the photodiodes as a function of the optical delay would lead to a measurement overwhelmed by the pulse-to-pulse intensity noise from the laser. There are a number of aspects added to the measurement aimed at reducing this noise, detailed below.

2.8.1 Averaging

It is reasonable to assume that, over timescales longer than the pulse repetition rate, the pulse intensity noise in the laser source is random and normally distributed. For this reason, we can reduce the noise a great deal by averaging the measurement over multiple pulses. The resulting averaged electric field measurement $E_{\text{av}}$ over $N$
Chapter 2: Terahertz time-domain spectroscopy

2.8 Reducing noise

Pulses is given by

\[ E_{av} = \frac{1}{N} \sum_{N} E_N \]  

(2.5)

A typical terahertz transient can be mapped out with a resolution of 0.05 ps/point in 100 separate measurements (each at a different optical delay). Clearly the benefit to the noise level from averaging extra pulses diminishes with the increasing number of pulses acquired, however the only real constraint on the noise reduction from averaging is the acquisition time for each data point. Given that the laser repetition rate is limited to 1 pulse per millisecond, averaging over 100 pulses per field measurement results in acquisition times of around two minutes for each terahertz transient. For samples exhibiting very low transmission, acquisition times can be considerably longer and are limited only by the long-term operating stability of the laser.

Averaging time scales

In the measurement algorithm used for our spectrometer there are two methods in which averaging can be implemented. The first is averaging at every electric field measurement point; this averaging is carried out by the lock-in amplifier and yields the average output over 100 or more consecutive laser pulses. The second averaging process is carried out in the spectrometer control software and involves repeating each time-domain sweep multiple times and averaging the sweeps - the separation between each averaged sweep is usually several minutes. Although mathematically identical, the two averaging processes take place over different time scales. Long-term averaging by repeating sweeps is important when multiple long duration measurements are taken over the course of a set of experiments, as fluctuations in laser
output power might occur over the timescale of minutes or even hours. However long-term averaging is relatively inefficient as it requires extra time for the delay-line to move between points. In most measurements a combination of the two strategies is used with a short time (100 ms) spent averaging each electric field point, and each sweep repeated until the noise level is acceptably low.

2.8.2 Modulation and phase-sensitive detection

A widely used strategy for noise-reduction throughout experimental physics is to modulate the measurement at a known frequency with fixed phase, and to use a phase-sensitive detector to pick out only components of the detection signal which are modulated at this frequency. In the terahertz spectrometer we can modulate the arrival of pulses in the terahertz generation beam using a mechanical chopper, locked in to the repetition frequency of the laser amplifier. The chopper is set to modulate at half the laser repetition frequency, giving pulse-on, pulse-off modulation. A narrowband notch filter in the lock-in amplifier ensures we only measure the component of the photodiode output which is changing with the arrival of terahertz generation pulses; the filtered signal is then multiplied by a phase-shifted signal oscillating at the modulation frequency. These two stages reject any background signal which is not at the same frequency as the modulation; the phase of the lock-in reference signal can be adjusted to give the maximum output signal for a given terahertz field measurement.
2.8.3 Differential gain

Modulation and phase-sensitive detection do not remove all intensity noise between the pulses - successive pulses from the laser will be of slightly varying intensity, leading to noise in the terahertz signal; such noise cannot be eliminated by modulation as it is synchronised with the laser pulse repetition rate. The differential detection scheme eliminates some of this noise by rejecting any signal which is common to both photodiode channels. For example, a single anomalously high intensity pulse will provide an equal amount of extra signal on the positive photodiode channel as on the negative photodiode channel; if the channels are well-balanced the noise will be cancelled electronically.

Circuitry to remove this noise must also amplify the signal from the photodiodes and stretch it in time. The pulses arriving at the photodiodes are much shorter in duration than the photodiode rise time (typically of around 10 μs duration) so after a rise-fall cycle of the diodes we have an electronic signal of just microseconds covering a millisecond measurement interval. Circuits to amplify and stretch the signal before reaching the lock-in amplifier must have well-chosen designs for optimising common-mode rejection, gain, noise-rejection and tolerance to parameters such as a mismatch between the electronic response of the two photodiodes. In Fig. 2.5 we show a succession of designs of increasing sophistication, all of which have been used at some stage in the work for this thesis.

Fig. 2.5(a) shows a very simple design in which the diodes are placed back-to-back, with the amplifier being a simple voltage amplifier in which the gain and time-constant can be set by adjusting R1 and C1. The diodes act as independent voltage sources, and as long as the intensity is matched on each diode only the differential
Figure 2.5: Circuits used for amplified differential photodiodes: (a) No common mode rejection (b) Instrumentation amplifier (c) Instrumentation amplifier with signal and hold.
Reducing noise

signal between them will be amplified. It is relatively straightforward to add gain to this circuit, which is only limited by the specifications of the operational amplifier chosen. The primary disadvantage is for the case of poorly matched photodiodes - if the response times of the diodes are not identical then for some of the rise-fall period of the voltage the subtraction between the diodes will be inexact, compromising the noise rejection. Additionally, the high common-mode rejection of the op-amp is unused, and the photodiodes are used as voltage sources rather than current sources, which is conventionally bad practice in the case of high-intensity light pulses.

Adding a pre-amplifier to each photodiode before the subtraction should allow us to benefit from the common-mode rejection of the op-amp - a circuit designed for this is shown in Fig. 2.5(b), which is a standard differential instrumentation amplifier design. Here we have two non-inverting amplifiers feeding in to a third differential amplifier before the output. This circuit improves common mode-rejection a great deal, and by replacing R2a with a variable resistor we can compensate for any mismatch between the two inputs. However, optimising this circuit for high gain and good temporal stretching of the signal is difficult, mainly due to the high-intensity, short-duration pulses which constitute the input. Stretching the pulses to a long duration in the pre-amp stages gives high voltages to the differential stage, which saturate the op-amp. If the temporal stretching is carried out in the differential stage the differential gain is compromised. Once realistic component values are chosen for Fig. 2.5(b) the performance of the circuit in the spectrometer is only marginally improved above the simple circuit of Fig. 2.5(a).

All of the above problems are solved in Fig. 2.5(c) which incorporates a signal/hold circuit in to the instrumentation amplifier. In this design the main amplifier can be optimised for differential gain without concern for the temporal stretching.
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2.8 Reducing noise

The signal/hold chip simply samples the output of the amplifier at the point of pulse arrival (using a trigger system) and produces it at the output for the entire 1 ms duration of the signal period. A unity-gain amplifier on the output is to enhance the output of the signal/hold chip to drive the high impedance input of the lock-in amplifier. The only disadvantage in this circuit design is the relative complexity in building and optimisation; using this circuitry it is possible to measure terahertz pulse traces with signal to noise levels in excess of 8,000:1 with acquisition times of less than two minutes.

2.8.4 Control software

Software on the PC (Fig. 2.3) controls the movement of the motorised translation stage and performs acquisition of data from the lock-in amplifier, as well as averaging. The system is interactive, programmed using National Instruments Labview version 7.1. For a data acquisition sweep, the algorithm moves the translation stage by a set step size (typically 7.5 µm, corresponding to 0.05 ps of optical delay) and then records the voltage output of the lock-in amplifier after waiting 100 milliseconds for the output to settle on an averaged value. After all the time-steps are complete the program returns the delay line to its starting position. Repeating the sweep multiple times allows for long-term averaging (in addition to the averaging over 100 pulses taken by the lock-in amplifier in each acquisition point); the control software repeats the scan a pre-set number of times and generates two data files - one containing the average of readings from all sweeps, and one containing the non-averaged raw data for diagnostic purposes.
2.9 Environment control

The existence of numerous rotational and long-range vibrational molecular resonances in the terahertz range is one of the motivations driving technological applications - however, the same modes can cause interference with other measurements. In particular, the water vapour found in the atmosphere has numerous strong, narrow rotational modes in the range 0.1-3 THz. In principle the spectral features of these modes can be normalised out from transmitted spectrum as part of the instrument response - however in practice many of them are too strongly absorbing and highly sensitive to the humidity of the laboratory, which can change rapidly. The solution is to flush the terahertz path with an atmosphere of either pure nitrogen or dried air; the humidity is monitored using a commercially available sensor. For this purpose a sealed box is built around the terahertz path of Fig. 2.3 with glass windows to allow entry of the terahertz generation beam, terahertz detection beam and optical pump beam.

2.10 Terahertz pump-probe

It is possible to change the properties of many materials using pulses of light - a common system is the photogeneration of charge carriers in silicon or other semiconductors. This method of manipulating material properties is particularly interesting as it can be used to make fast, dynamic changes to a sample - leading directly to applications in building all-optical switches or intensity modulators. A technique well suited to exploring optical control over material properties is optical-pump, terahertz probe spectroscopy. In this technique high energy pulses of light (from
the same laser source used to generate and detect terahertz radiation) are used to photoexcite samples in the terahertz beam. The terahertz-range pulses are used as a probe of the transmission of this photoexcited structure. The large separation in wavelengths between the terahertz range and the NIR or blue wavelength pump pulses means that analysis of such experiments is relatively straightforward; the optical pump pulses will not generally interact with any structures designed to operate at terahertz wavelengths, and the interaction length of the optical pulse with most semiconductors is sufficiently short to be negligible in the terahertz range. Furthermore, as the optical pulses from the laser are extremely short, changes can be made to the material in the beam on sub-picosecond time scales.
2.10.1 Experimental methods

In Fig. 2.6 we show a schematic of the pump-probe scheme. An optical pulse arrives at the sample some time-delay *before* the terahertz pulse and photo-excites the sample. The terahertz pulse then transmits through the photo-excited sample and is measured using the electro-optic detection system described in section 2.6.

The pump beam (pathway shown in Fig. 2.3) can actually comprise more than 90% of the laser output intensity - typically, a total of 1.0 W of laser power is taken for the spectrometer (with the rest of the 3.0 W amplifier output used to drive independent experiments), with 900mW used in the pump beam, 60mW in the terahertz generation beam, and the remainder used for terahertz detection. Once the pump beam is split away from the laser output, it is run into a motorised optical delay line - the arrival of the pump pulses at the sample must be synchronised to the arrival of the terahertz pulses, with many experiments requiring that the pump pulse arrive more than 20 picoseconds before the terahertz probe. After the delay line, we can change the wavelength of the pump beam using a BBO crystal through frequency up-conversion.

2.10.2 Frequency upconversion

Eqn. 2.2d has, as well as a frequency-subtraction component, an additive \((\omega_1 + \omega_2)\) component. Beta barium borate (BBO) has a high \(\chi^{(2)}\) coefficient in the sum-frequency range of the 800 nm pulses, leading to efficient combination of two IR photons to yield one photon of blue 400nm light. Conversion efficiency can be as high as 20%. There are many reasons for requiring shorter wavelength pump pulses, in particular for experiments on silicon where the penetration depth changes from
microns at 800nm to sub-micron\textsuperscript{11} at 400nm.

### 2.10.3 Referencing and normalisation

Addition of the pump pulse to the measurement necessarily introduces noise to the terahertz trace as the transmission through the sample will vary with the intensity of the pump beam. Furthermore, high-intensity photomodulation can almost eliminate the terahertz transmission of the sample. For this reason we use a slightly different modulation and referencing scheme, detailed below.

Firstly, we take a reference measurement of transmission through the un-photoexcited sample, $E_{\text{ref}}(t)$, with the optical chopper in the terahertz generation beam as in a conventional terahertz measurement, with the optical pump beam blocked. Then, we shift the chopper to the optical pump beam and photoexcite the sample. Because we are now using pulse-on, pulse-off modulation with the *pump* beam, the electric field measurement is now of the change in terahertz electric field induced by the pump pulse, $\Delta E_p(t)$. From these two measurements we can find the actual terahertz transmission through the photoexcited sample by

$$E_{\text{trans}}(t) = E_{\text{ref}}(t) - \Delta E_p(t)$$

The result of this technique is that we can measure very small levels of terahertz transmission, with minimal compromise to the noise level from the introduction of the pump beam. This is because the rapid pulse-on, pulse-off modulation of the pump beam will allow us to at least partially cancel the relatively slow ‘noise’ oscillations introduced by the pump, as we shall demonstrate below.

Consider that the terahertz electric field at some point in time, $E$, has some
random noise component $\delta E$ added to it - the total measured signal being $E_{in} + \delta E$, where the noise component is of unknown magnitude and sign. The transmitted terahertz field, $E_{trans}^0$ is given by the product of the transmission coefficient $t_0$ of the unphotoexcited sample and the incident field $E_{in}$:

$$E_{trans}^0 = t_0 \cdot (E_{in} + \delta E) \quad (2.7)$$

Both noise and transmitted field are scaled by the transmission coefficient, meaning the relative noise is completely independent of the transmission coefficient.

In the case of photoexcitation, there is now also some random variation $\delta t_p$ in the transmission coefficient of the photoexcited sample ($t_p$). Now the total transmitted field is given by

$$E_{trans}^p = (t_p + \delta t_p) \cdot (E_{in} + \delta E) \quad (2.8)$$

meaning that the total transmission noise is given by $\delta t_p \cdot \delta E + \delta t_p \cdot E_{in} + \delta E \cdot t_p$, with the $\delta t_p \cdot \delta E$ component being negligibly small. Noise in the transmitted field now scales with incident electric field; for this reason the noise level will be greatly increased above that for unphotoexcited transmission spectra.

In photoexcitation experiments we typically want to measure the change in terahertz electric field upon photoexcitation, $\Delta E$. This can be achieved by taking two measurements of $E_{trans}$, with and without the pump beam:

$$\Delta E = E_{trans}^0 - E_{trans}^p \quad (2.9a)$$

Adding noise:

$$\Delta E = (E_0 + \delta E_0) - (E_p + \delta E_p) \quad (2.9b)$$
We can again consider the transmission noise and electric field noise - however we now have two electric field noise levels $\delta E_1$ and $\delta E_2$ corresponding to the noise on the different sets on input terahertz pulses (one with and one without the pump beam).

\[
\Delta E = (E_{in} + \delta E_1) \cdot t_0 - (E_{in} + \delta E_2) \cdot (t_p + \delta t_p) 
\]

\[
\Delta E = E_{in}(t_0 - t_p) + \delta E_1 t_0 - \delta E_2 t_p + \delta t_p E_{in}. 
\]

As with the regular transmission measurement we can take the average over $N$ pulses.

\[
\Delta E = \frac{1}{N} \sum_N E_{in}(t_0 - t_p) + \frac{1}{N} \sum_N (\delta E_1 t_0 - \delta E_2 t_p) + \frac{1}{N} \sum_N \delta t_p E_{in} 
\]

The crucial factor in the overall noise level is the degree of correlation between $\delta E_1$ and $\delta E_2$. Suppose that the two terahertz pulses measured are taken several minutes apart - one could reasonably infer that the magnitude and sign of the noise signal on each pulse would be largely uncorrelated. However, if we measure the noise level on two sequential pulses from the laser, we might suppose that the magnitude and sign of the noise level on the pulses would be strongly correlated, as the intensity output of the laser varies on the timescale of multiple pulses. By using the optical chopper to modulate the pump beam we have effectively changed our pulse-on / pulse-off measurement to being with photoexcitation / without photoexcitation. We are switching rapidly between measuring with $t_0$ and $t_p$. This means that now, $\delta E_1 t_0$ and $\delta E_2 t_p$ in Eqn. 2.10c are not independent measurements made several
minutes apart, but are the noise level on two sequential terahertz pulses. Because the measurement is subtractive at this point, the noise points will cancel in the majority of cases. This partially removes the term \((\delta E_{1t} - \delta E_{2t})\) in Eqn. 2.10c. Because of the \(\delta t_E\) term in the same equation, the measurement of a photoexcited sample will still be somewhat noisier than a regular transmission measurement, however this is partially offset by the new modulation scheme.

An alternative way of considering the pump-probe modulation scheme is in terms of the \(1/\nu\) distribution of random noise in which the largest noise variations are found at the longest time periods. Because of this distribution it makes sense to modulate the experiment as quickly as possible - hence the pulse-on, pulse-off modulation used in the regular terahertz transmission experiment. In the experiment with the extra source of noise in the form of the pump beam intensity variations, it makes sense to modulate the arrival of pump pulses as rapidly as possible too.

### 2.11 Conclusions

We have considered in some detail the techniques of terahertz time-domain spectroscopy used in this thesis. This has included a brief survey of terahertz generation methods, an explanation of the electro-optic detection scheme used, a number of strategies for reducing noise. Finally we have discussed pump-probe spectroscopy using visible-wavelength pulses to photo-excite a sample followed by a terahertz pulse to probe the electromagnetic response.
Chapter 3

Subwavelength slits

Summary

In this chapter we present measurements and numerical modeling which elucidate the role of surface plasmons in the resonant transmission of a subwavelength slit in a conducting material. Using THz-time domain spectroscopy, we determine the Fabry-Pérot transmission resonances for a single slit formed from a wafer of a semiconductor with a surface plasma frequency in the THz frequency range. We measure large red-shifts in the resonant frequencies close to the surface plasma frequency, approaching 50% lower than the resonance frequencies expected well below the surface plasma frequency, an effect attributed to the coupling of plasmons on the adjacent surfaces of the slit. Using the phase-information from terahertz time-domain spectroscopy we can measure the effective index of the surface plasmon in the slit, and compare it to an analytical model.

3.1 Background

3.1.1 Previous work

In 1999 it was shown that an array of subwavelength slits in a metal film\textsuperscript{59} could exhibit enhanced optical transmission in a similar fashion to the enhanced transmission that was observed for a (more complex) array of holes by Ebbesen et al.\textsuperscript{60}
in 1998. Subsequently, this enhanced transmission through slits was demonstrated experimentally at optical\textsuperscript{85} and microwave frequencies\textsuperscript{86}. Ensuing theoretical work has determined factors which dictate the frequency of resonance transmission\textsuperscript{87} and shown the effects of slot size and incident light angle\textsuperscript{88}, as well as having calculated the levels of field enhancement in slit arrays\textsuperscript{89}. Experiments have demonstrated slit-based transmission enhancement in the terahertz range\textsuperscript{90} and have shown that the transmission of a single slit can be enhanced still further through the imposition of surface structure\textsuperscript{66}.

### 3.1.2 Fabry-Pérot resonances

In most of the literature considered above, the structures can be categorised as either individual isolated slits or slit arrays. For arrays of slits the periodicity of the array can (but does not always) influence the resonant transmission, whereas for the isolated case only the slit dimensions and material properties influence the resonance characteristics. It is the latter case of an isolated slit which we consider in this chapter. In the isolated slit system the ‘dimension’ which supports the transmission resonance is the length of the slit, which forms a Fabry-Pérot-like resonant cavity.

A Fabry-Pérot resonance refers to a cavity-based electromagnetic resonance, and is named from Charles Fabry and Alfred Pérot who showed such an effect for the first time in the late 19th Century\textsuperscript{91}. In the original experiment radiation formed near-standing wave modes between two partially transmitting mirrors; the impedance mismatch between the dielectric cavity and the metallic mirrors leads to mode quantisation inside the cavity. In this case the boundaries at the edge of the mirror cavity are minima in the electric field of the cavity mode. An important distinction which
**Figure 3.1:** Comparing the electric field boundaries in a classical Fabry-Pérot (top) and the quantised mode in a subwavelength slit (bottom).
must be made is that in a slit system, the plasmonic mode inside the slit has higher effective index than the free-space radiation outside the slit, and the electric field boundaries are maxima in the electric field, as illustrated in Fig. 3.1.

As we know that an approximately half-integer number of wavelengths will be quantised along the length of the slit at resonance, we can predict the frequency of the resonances $\nu_{FP}$ using:

$$\nu_{FP} = \frac{nc}{2l}$$  \hspace{1cm} (3.1)

where $l$ is the length of the slit and $n$ is an integer. For a slit in a slab of perfect metal (a material with infinite conductivity at all frequencies), it has been shown that Equation (3.1) provides an accurate estimate of the resonant transmission frequencies - provided that the slits are very narrow compared to the wavelength of the transmitted radiation.$^{87,93}$

However, for the case of narrow slits in real conductors with finite conductivity, the modes within the slits are coupled surface plasmons (SPs), and one obtains very large red-shifts.$^{59,94}$ from the resonant transmission frequencies predicted by Eq. (3.1). Resonant slit cavities feature in many photonic structures, many of which have potential applications, in sensing or spectroscopy.$^{88,95,96}$ It is therefore important to understand the role of SPs in influencing the resonant behaviour of this fundamental system.

### 3.2 Motivation and approach

Our goal in this work is to find the role that the permittivity of the conductor in which the slit is formed plays in determining the position and width of the reso-
nances. In particular, the interplay between the slit end-effects and the propagation characteristics of the surface plasmon modes inside the slit means that the mode position can be a complicated function of slit width. Earlier work in the microwave frequency range\textsuperscript{92} on slits formed in a plate of metal showed that an analytical consideration of the mode position\textsuperscript{87} was problematic as the system is highly sensitive to the finite conductivity of the metal in which the slit is formed, even at microwave frequencies for which metals are good conductors. Our approach in this work is to observe slit resonance behaviour both at high conductivity and near the plasma frequency in a single measurement - we can do this by covering a broad frequency range (using terahertz time-domain spectroscopy) and using a material with rapidly changing dielectric function in this frequency range (InSb).

Indium Antimonide (InSb) has a surface plasma frequency ($\omega_{sp}$) of around 1.7 THz\textsuperscript{1,97}. For narrow slits in the InSb we find that, near the surface plasma frequency, resonances are red-shifted by more than 50\% from the values predicted by equation (3.1) - this frequency shift is more than two orders of magnitude larger than the shifts reported in metals at low frequencies\textsuperscript{92}. By measuring the phase delay of the transmitted radiation we demonstrate that the coupling of SPs on the surfaces within the slit modifies the effective index of the mode within the cavity and hence the frequency of resonant transmission, an effect which becomes significantly stronger for frequencies approaching the surface plasma frequency.

### 3.3 Material parameters

Semiconductors have remarkably tunable dielectric functions. We choose a semiconductor with a surface plasma frequency in the THz range, so that the THz dielectric
function is similar to that of metals at visible/ultraviolet frequencies. The dielectric function, $\varepsilon(\omega)$, of InSb in this frequency region can be approximated using the Drude model:

$$
\varepsilon(\omega) = \varepsilon_{\text{lattice}} - \frac{\omega_p^2}{\omega^2 + i\omega\gamma}
$$

(3.2)

In this model, $\varepsilon_{\text{lattice}}$ is the zero frequency permittivity of the semiconductor, $\omega_p$ is the plasma frequency of the conductor and $\gamma$ is the scattering frequency. In Fig. 3.2 we plot the room temperature dielectric function for typical InSb wafers using Drude parameters from the literature$^{97}$, with $\gamma \approx 0.8 \times 10^{12}$ radians/s and $\omega_p \approx 40 \times 10^{12}$ radians/s. Below we will refine the values of the Drude parameters for the samples of InSb used in our measurements.

Fig. 3.2 shows the large change in the dielectric function of InSb across the THz frequency range. The surface plasma frequency for a conductor-air interface is defined$^{26}$ as the frequency at which $\varepsilon_{\text{real}} = -1$, and represents the high-frequency cut-off for a SP mode propagating on that interface$^{55}$ (section 1.3.1). The imaginary
component of the dielectric function for InSb, which determines loss, is relatively small in this frequency range. In order to obtain $\omega_{sp}$ in the THz frequency range, other common semiconductors must be heavily doped. For example, to obtain $\omega_{sp} = 2.0 \text{ THz}$, for n-doped GaAs$^{98}$, $\omega_p = 45$ and $\gamma = 3.9 \text{ radians/s}$. Similarly for n-doped Silicon$^{99}$ with $\omega_{sp} = 0.7 \text{ THz}$, the Drude parameters are $\omega_p = 17$ and $\gamma = 5.2 \text{ radians/s}$. In general, higher scattering rates will lead to SPs with shorter propagation length for a given surface plasma frequency.

3.4 Sample preparation

Semiconductor wafers can be an exceptionally convenient substrate for terahertz experiments not only because of their interesting material properties but also because of their dimensions. Typically, commercially available wafers have thicknesses from 100 $\mu$m to 900 $\mu$m, exactly the length-scale of the terahertz wavelength range.

In this experiment we form the slit aperture in an undoped wafer of InSb with DC conductivity at 77K of approximately 2400 Sm$^{-1}$ and a thickness of 456 $\mu$m. The aperture is formed by cleaving a mono-crystalline wafer of InSb along a crystal plane using a diamond scribe. This cleaving technique is well known in small-scale semiconductor wafer processing$^{100}$, and can be used to produce very flat edges as the ‘cracking’ of the wafer tends to follow a crystal plane. This can be achieved by making a $\approx$1mm scratch on the edge of the wafer, aligned in the approximate direction of a crystal plane - the crystal plane direction is inferred from the orientation of the wafer flat-edge. The wafer is then broken over a sharp edge aligned parallel to the scratch underneath the wafer. A single crack is formed from the scratch and the wafer breaks in to two parts.
For alignment the wafer parts are mounted on a single polished glass slide with contact adhesive; the slide is then cut so that wafer is exposed on both sides for one centimetre either side of the break. The two interfaces are aligned parallel to each other under a microscope, mounted on to micrometer translation stages so that the width $w$ of the slit is variable and placed near the focus of a conical beam in a THz spectrometer. The resulting slit is defined by length $l$ and width $w$ - see Fig. 3.3. Under an optical microscope the sides of the slit are observed to be flat to within a few microns across its length. No point defects are visible under an optical microscope, and the wafer interfaces are cleaned in-situ using isopropanol to remove any stray adhesive. The precision of the micrometer stages is such that the slit size can be controlled within 5 $\mu$m.

3.5 Transmission measurements
3.5 Transmission measurements

**Figure 3.4:** Time domain electric field of a THz pulse measured in the far-field after transmission through a 30 µm wide aperture; the reflected pulse, which has made one round-trip of the slit length $l$ is indicated. Also shown is the reference pulse, amplitude scaled down by a factor of 10.

### 3.5.1 Polarisation

The transmission of the slits is measured with incident THz radiation polarised normal to the slit. In general the polarisation of the incident radiation must be TM with respect to the planes of top and bottom slit interfaces in order to excite SPs within the slit and observe resonant transmission; there are however some special cases in which TE modes can be supported within a subwavelength slit through inclusion of a high index dielectric material inside the cavity\(^{101}\). Here we only consider the case of air-filled slits with incident radiation polarised normal to the slit direction. All the slit sizes used are too small to support any TE cavity modes.
3.5.2 Time-domain spectroscopy

THz-TDS enables us to map out the electric field of a single-cycle THz pulse as a function of time, using the spectrometer described in Chapter 2 with the addition of two extra parabolic mirrors to focus and re-collimate the terahertz radiation. The slit sample in this experiment is placed at the focal point. The far-field electro-optic sampling in the detection method yields a time domain electric field profile of the radiation transmitted through the slit (such as that plotted in Fig. 3.4) which can be converted to the frequency domain by means of a Fast Fourier Transform, yielding the complex electric field as a function of frequency, \( E(\omega) = A e^{i\phi} \). Because the measurements are fully time-resolved it is possible to extract both the amplitude \( A \) and phase \( \phi \) of each frequency component. Normalised transmission intensities are found by dividing the spectral intensity transmitted through the sample by a free-space reference intensity; \( T(\omega) = (A_{\text{trans}})^2/(A_{\text{ref}})^2 \). We also calculate the effective refractive index of the slit using the phase shift between reference and sample spectra, \( \Delta \phi = \phi_{\text{trans}} - \phi_{\text{ref}} \), through the relation \( n_{\text{effective}} = n_0 + \Delta \phi c/\omega l \), where \( n_0 \) is the index of the reference medium (in this case air, \( n_0 = 1 \)) and \( l \) is the length of the slit.

3.5.3 Transmission spectra

Time domain transmission through a slit in InSb is shown as Fig. 3.4. We firstly observe the initial THz pulse that is transmitted directly through the slit followed by a smaller time-delayed pulse - this is a reflected pulse that has made one round-trip of the slit. In Fig. 3.5(a) we plot the normalised intensity transmission spectrum as a function of frequency. The numbered transmission peaks on these figures indicate
Figure 3.5: (a) Measured normalised transmission intensities for a slit in InSb for varying slit width $w$ from 10-90 $\mu$m. Numbered peaks label the order of the corresponding FP-like transmission. (b) Example of a finite-element modelled spectrum through an InSb slit at $w = 40\mu m$. 
quantised FP peaks resulting from the cavity reflections. It should be noted that the first mode is at the very limit of the lowest measurable frequency for the THz spectrometer, and as such has a higher level of experimental error. Note that the observed peaks are considerably shifted from values predicted by Eq. (3.1). The first five FP modes are clearly observed, and the higher order peaks are seen to broaden and decrease in amplitude as they approach the surface plasma frequency.

### 3.6 Finite element modelling

We construct a finite element model of the InSb slit using Ansoft HFSS, which is described in section 1.6. In this model we treat the slit as being of infinite...
breadth in the $y$ direction (see Fig. 3.3) by imposing perfect H-field boundaries on both sides of the model; the unit cell for this infinitely repeating section is 30 $\mu$m across. In order to reduce the computational complexity by a factor of two, the slit is treated as being symmetrical from top to bottom - a Perfect E boundary is imposed on the top of the slit in the $x - y$ plane. All other model boundaries are far-field radiation boundaries. Mesh operations are used to impose a maximum tetrahedra size of 10 $\mu$m inside the InSb - this increases the accuracy of the resulting transmission spectra as it devotes more calculation time to the parts of the SP field which penetrate the InSb than would be allocated by the automatic meshing algorithm; as the fields inside the conductor are very low the automated meshing does not allocate tetrahedra to the region even though the fields in this region influence the overall transmission very heavily. The excitation used is a plane wave with wavevector incident in the $z$ direction and electric field is polarised normal to the slit direction as in the experiment. The finite element model is analysed in a similar way to the experimental results - total transmitted intensity from the modelled slit is calculated in a far-field plane 3mm distant from the slit exit, and is normalised against the electric field incident on the slit.

We compare the finite element model to the measured transmission spectra in Fig. 3.5(b). To obtain the best agreement between measurement and model we vary the InSb Drude parameters used in the model: the best fit is obtained with $\omega_p = 46 \times 10^{12}$ radians/s, and scattering frequency $\gamma = 0.63 \times 10^{12}$ radians/s. We take the lattice permittivity $\varepsilon_{\text{lattice}}$ to be $1.5$. These values are comparable with published values of InSb Drude parameters - any small deviation amongst reported values is readily accounted for by variation in impurity density between InSb samples.
3.6.1 Field plots

In Fig. 3.6 we show a cross-section of the $x - z$ plane of the slit, overlayed with the electric field magnitude calculated by the finite element model at 0.5 THz - this corresponds to the peak of the second order mode. Electric field maxima can be seen at the slit entrance and exit, as well as one region of high field inside the slit. Regions of very high field (red) can be seen at the corners of the slit, caused by scattering at the sharply pointed edges of the InSb wafer. This field plot shows that the slit transmission resonances do indeed correspond to Fabry-Pérot-like modes inside the slit cavity, and the plot provides evidence for the kind of field distributions described in section 3.1.2. The colour scale in this plot does not show the fields of the coupled plasmons inside the slit extending in to the InSb as the field intensity inside the conductor is much lower than in the air regions.

3.7 Resonance position

On changing the width of the InSb slit aperture it is clear from the transmission spectra in Fig. 3.5(a) that the resonance peaks shift to lower frequency as the aperture width is decreased. In order to show the degree to which the frequency of each resonance moves, we plot in Fig. 3.7 the position of each resonance peak as a function of slit aperture size. The frequency of the peak position ($\nu_{\text{mode}}$) is normalised to the corresponding FP frequency, given by Eq. (3.1) - we plot $\nu_{\text{mode}}/\nu_{\text{FP}}$. The slit width is scaled by the FP transmission wavelength ($w_{\text{slit}}/\lambda_{\text{FP}}$), giving a fully normalised plot that shows the fractional change in resonant frequency against the width of the slit compared to the resonance wavelength. Such normalisation is necessary in order to compare shifts in frequency across such a wide frequency
Figure 3.7: Plot of normalised resonance frequencies, $\nu_{\text{mode}}/\nu_{FP}$, against normalised slit width, $w/\lambda_{FP}$, for modes 2 to 5 in an InSb slit. Solid lines are results of finite element modelling, markers are the results of measurements. The dashed lines show the results of finite element modelling of a slit with the same dimensions formed in aluminium.
range.

Fig. 3.7 shows that the frequency of all the transmission resonances decreases for smaller slit widths, with measurements indicating shifts of around 50% from the frequencies predicted by Eq. (3.1) for slits of $w/\lambda_{FP} \leq 0.02$. The plot also illustrates a change in behaviour between modes dependent on their proximity to the surface plasma frequency. Higher order modes, with resonances closer to $\omega_{sp}$, drop in frequency for slit widths which are a much larger fraction of the resonance wavelength. For example, the second order mode starts to decrease in frequency for normalised slit widths of $w/\lambda_{FP} < 0.16$, whereas the fifth order mode drops in frequency for slits of $w/\lambda_{FP} < 0.4$

For transmission of a slit in conducting material, there are two effects which give rise to shifts in the resonant frequencies from those predicted by Eq. (3.1). Firstly, it is known that the boundary conditions at the slit entrance and exit lead to a phase shift between light propagating inside the slit and the free-space radiation either side of it - an analytical formulation is given by Ref. 93. This effect, which is important even for slits in highly conducting materials (i.e those materials with a surface plasma frequency considerably higher than the frequency of the incident light) results in a decreasing resonance frequency for increasing slit width$^{92,93}$ - this effect explains why $\nu_{\text{mode}}/\nu_{FP}$ does not tend towards 1 for large slits in Fig. 3.7. A second effect arises from coupling of SPs on the internal interfaces of the slit$^{59,94,102}$, which gives rise to an increase in the effective index for the cavity mode, and therefore a decrease in resonance frequency for decreasing slit width. Approximate analytical expressions for this effect (which are valid in the case of $w \ll \lambda$) are given by Refs.$^{102}$ and$^{103}$. It is clear from Fig 3.7 that the coupling of SPs has a pronounced effect on $\nu_{\text{mode}}/\nu_{FP}$ for narrow slits.
3.8 Effective index

Utilising the phase-shift information $\Delta \phi$ of our measured THz spectra, we can plot in Fig. 3.8(a) the effective index for InSb slits, using the methods described above. First, for all the traces in Fig 3.8(a) we observe some small peaks in the effective index, corresponding to peaks in the transmission spectrum Fig. 3.5(a). These are due to the interference on resonance of directly transmitted light with light which has made at least one round trip of the slit cavity. More significantly there is a large change in the effective index near the surface plasma frequency. For smaller slit widths ($w \leq 20 \mu m$), the effective index appears asymptotic to the surface plasma frequency - this behavior can be seen in the effective index plots for 10 and 20 $\mu m$ slits shown in Fig. 3.8(a). For very small slits ($d \leq 20 \mu m$) the transmitted intensity above the surface plasma frequency is very small, such that our phase measurements above $\omega_{sp}$ are erroneous. For larger slit widths ($w \geq 40 \mu m$) the effective index returns to unity above the plasma frequency due to a small intensity of non-resonant transmission.

The transmission through a conducting slit in the limit of very narrow widths is mediated by coupled SPs on the opposite sides of a conductor-insulator-conductor structure. The complex propagation constant and, therefore, the effective index of refraction and the attenuation length of this mode can be calculated analytically. The fundamental equation for the surface plasmon propagation in a finite-thickness slab (thickness $w$, permittivity $\varepsilon_2$) bounded by two semi-infinite media (both with permittivity $\varepsilon_1$) is given by

$$\tanh(\alpha_2 w) = -\frac{2\varepsilon_2 \alpha_2 \varepsilon_1 \alpha_1}{\varepsilon_1^2 \alpha_2^2 + \varepsilon_2^2 \alpha_1^2}$$  \hspace{1cm} (3.3a)
Figure 3.8: (a) The measured effective index of InSb slits with aperture widths $w$ from 10 to 70 $\mu$m. The effective index of the 10 and 20 $\mu$m slits increases rapidly approaching the surface plasma frequency. (b) Theoretically calculated values of the effective index of InSb slits of varying width $w$. (c) The calculated propagation length of the coupled SP inside the InSb slits for various slit widths $w$. 
which is expressed as a function of the propagation constants $\alpha_1$ and $\alpha_2$:

$$\alpha_i = k_{sp}^2 - k_0^2 \varepsilon_i, \quad i = 1, 2$$

(3.3b)
as is shown in Fig. 3.9. Solving equation 3.3 exactly for $k_{sp}$ is only possible by making approximations such as assuming small $w$ or very large surface plasmon wave-vector. As we need to compare to results for a wide range of slit widths over a broad frequency range we must resort to a numerical solution in which Eqn. 3.3 is solved by varying $k_{sp}$ and minimising the difference between the two sides of Eqn. 3.3a. The permittivity of InSb is taken from the Drude model using the same parameters as for the finite element model of section 3.6, and the permittivity of the slit core is taken to be unity (for vacuum). Once $k_{sp}$ is determined we can find the effective index of the mode by

$$\Delta k = k_{sp} - k_0$$

(3.4a)
Chapter 3: Subwavelength slits

\[ n_{\text{effective}} = n_0 + \Delta k\frac{c}{\omega}, \]

(3.4b)

essentially in the same manner as for the experimental data. We can also calculate the propagation length of the surface modes in the slit \( \delta_{sp} \) by:

\[ \delta_{sp} = \frac{1}{2\Im(k_{sp})}. \]

(3.5)

The results of these calculations are plotted as a function of frequency in Figs. 3.8(b) and 3.8(c) for different widths of the slit. Similarly to the measurements (Fig. 3.8(a)), the effective refractive index increases as the width of the slit is reduced and as the surface plasma frequency is approached from the low frequency side. This increase is due to greater penetration of the electromagnetic field into the conductor, which also causes the concomitant reduction of the surface plasmon propagation length due to ohmic losses. The agreement between the experiment and analytic model is not perfect owing to defects inside the slit generated by sample machining which ‘smear out’ the measured phase-change. The calculations in Figs. 3.8(b) & 3.8(c) fully explain the general behaviour of the FP resonances on approaching the surface plasma frequency - the rapid change in effective index accounts for the shift in peak position, whilst the change in propagation length accounts for the broadening of the resonance peaks.

3.9 Comparison to metals

The coupling of SPs has been shown to play a role in determining the transmission of a conducting slit aperture even for frequencies well below the surface plasma frequency of the slit material (e.g. aluminium at microwave frequencies\(^92\)). For metals,
surface plasma frequencies are typically in the UV region of the spectrum\textsuperscript{1}. Using Finite Element modelling we compare the behaviour of resonant transmission through our InSb slit to the behaviour of an Aluminium slit of the same dimensions, across the same frequency range - the normalised resonance peak positions from this modelling are plotted as dashed lines in Fig. 3.7. The traces show that the position of each resonance in Aluminium slits does red-shift for very narrow slit widths. However the shift in Aluminium resonances occurs for much narrower slit widths than for the slits in InSb. Typically, the frequency drop is present in Aluminium slits for $w/\lambda_{FP} \leq 0.01$. These results can be compared to the measurements on the InSb slit, in which the fifth mode red-shifts for $w/\lambda_{FP} \leq 0.4$. This comparison emphasises that near the surface plasma frequency of the slit material, resonance shifts due to coupling of SP modes occur for slits more than two orders of magnitude larger than for highly conducting materials.

3.10 Conclusions

In conclusion, we have elucidated the effect of coupled surface plasmons on the FP-like transmission of THz radiation through slits in conductors. For narrow slits we demonstrate that very large red-shifts in the resonant FP frequencies may be expected near the surface plasma frequency, an effect attributed to the coupling of surface plasmons on the adjacent interfaces of the slit. These shifts must be accounted for in the design of devices that make use of resonant slit cavities, especially those in conductors close to the surface plasma frequency.
Chapter 4

Terahertz surface spectroscopy

Summary

By employing a combination of time-domain measurements and numerical calculations, we demonstrate that the semiconductor InSb supports a strongly confined surface plasmon (SP) in the THz frequency range. We show that these SPs can be used to enhance the light-matter interaction with dielectric layers above the semiconductor surface, thereby allowing us to detect the presence of polystyrene layers around one thousand times thinner than the free space wavelength of the THz light. Finally, we discuss the viability of using semiconductor SPs for the purposes of THz sensing and spectroscopy.

4.1 Background

One of the primary applications of surface plasmons at optical frequencies is for the purposes of spectroscopy. Early work noticed that very thin organic films could perturb the surface plasmon resonance at optical frequencies on gold\textsuperscript{105}, and showed that surface plasmons can be useful for gas detection\textsuperscript{53}. More recent work has developed surface plasmon detection schemes which are exceptionally sensitive to small changes in refractive index near the surface\textsuperscript{38,106} and can be used to monitor
more complicated processes such as binding events on biological surfaces\textsuperscript{54}.

These studies at optical frequencies cannot be adapted directly for lower frequencies such as the infrared or terahertz range because, as described in Chapter 1, the electric field confinement of a surface plasmon on a metal drops rapidly with decreasing frequency. Furthermore, the coupling techniques used to transform free-space light into a surface plasmon must be adapted or even completely redesigned to be useful at longer wavelengths. In this chapter we present an experiment demonstrating that the confined electric field of a semiconductor terahertz surface plasmon can be used to determine the permittivity of a low-index dielectric analyte.

4.2 Motivation

Due to its non-ionizing nature and the distinctive optical response of many molecules in the THz frequency range, there has been much recent interest in using THz radiation for chemical and biological analysis\textsuperscript{107–109}. However, with THz wavelengths ranging from 100-1000 $\mu$m, the diffraction limit for this long wavelength light means that it is difficult to measure small volume samples. Recent work\textsuperscript{44,110,111} has demonstrated that by propagating THz radiation along a metallic surface or waveguide it is possible to detect the presence of thin dielectric layers on the metal surface, by allowing the THz surface wave to traverse a greater length of analyte. The effectiveness of this type of measurement geometry has recently been demonstrated by the development of a THz bio-sensor for DNA binding\textsuperscript{7}.
Figure 4.1: The electric field associated with a surface plasmon on InSb is much more strongly confined to the surface than for the THz frequency surface eigenmode on gold.

4.3 Field confinement

Near the surface plasma frequency of a conductor (typically in the UV/Visible spectral region for most metals) a propagating surface plasmon (SP) can exhibit subwavelength confinement of electric field in the direction normal to a conductor-dielectric interface. This subwavelength field distribution enhances light-matter interactions with material in the region above the conductor surface - a property which has been utilized in the development of surface plasmon bio-sensors. In contrast, at frequencies well below the metal plasma frequency, SPs exhibit very weak field confinement. Semiconductors, on the other hand, exhibit a plasma frequency that depends on the conduction band electron density, so that the properties of semiconductor SPs can be tailored within the THz frequency range through doping and photo-excitation. In particular, narrow gap semiconductors such as InSb have an intrinsic electron density appropriate for supporting low loss, highly confined THz SPs at room temperature. Indeed, the dielectric function of InSb in the THz frequency range is remarkably similar to that of plasmon supporting metals such as gold and silver in the UV/visible frequency range.

In this chapter we present phase-resolved measurements which demonstrate that
it is possible to determine the optical properties of a sub-micron sized dielectric layer above an InSb surface using a propagating SP. We show that the SP on InSb is significantly more sensitive to the dielectric layer than surface modes supported on a gold substrate. Moreover, we show that sensitivity to the dielectric analyte increases significantly as one approaches the surface plasma frequency of InSb. We discuss potential applications of THz semiconductor SPs for the measurement of analytes of subwavelength dimensions.

4.4 Material parameters

We use the Drude model to approximate the dielectric function of the conductors (gold and InSb) in the THz frequency range;

\[ \varepsilon_c(\omega) = \varepsilon_{lattice} - \frac{\omega_p^2}{\omega^2 + i\omega \gamma}. \]  (4.1)

For gold, we use a plasma frequency, \( \omega_p \), of \( 1.2 \times 10^{16} \) rad/s and a scattering rate (\( \gamma \)) of \( 1.2 \times 10^{14} \) rad/s - these values are fitted from visible/IR data from Ref.\(^1\).
The lattice permittivity, $\varepsilon_{\text{lattice}}$, of gold is taken to be 9.1. At THz frequencies the permittivity of gold is very large and predominantly imaginary ($\varepsilon_c = -1.0 \times 10^4 + 1.6 \times 10^6i$ at 1.2 THz), so that THz surface electromagnetic mode is only weakly bound; using the Drude parameters above, we calculate that at 1.2 THz the decay length for the surface mode's electric field in to air above a gold substrate is expected to be 1.8 cm (see Fig. 4.1). For InSb we use $\varepsilon_{\text{lattice}} = 15.6$ and Drude parameters are $\omega_p = 46 \times 10^{12}$ rad/s and $\gamma = 0.3 \times 10^{12}$ rad/s. Drude parameters will vary considerably between samples of semiconductor owing to variations in impurity density. In this work we use parameters found to be accurate for previous work on InSb samples from the same wafers (Ref.115), which have a specified DC conductivity at 77K of 2400 Sm$^{-1}$.

The surface plasma frequency $\omega_{SP}$ (defined as the high-frequency cut-off for a SP propagating on a conductor-air interface), occurring when the real part of $\varepsilon_c$ is -1, is approximately 1.7 THz in InSb. Near $\omega_{SP}$, the electric field associated with the SP decays very quickly into the dielectric region above the surface (Fig. 4.1): in contrast to gold, the SP propagating on an InSb-air interface at 1.2 THz has a decay length into the air of only 178$\mu$m, less than 70% of the wavelength of free space radiation and two orders of magnitude smaller than the decay length for the surface mode on gold. We show below that this strong confinement of the electric field near the InSb surface enhances the light-matter interaction in the region near the surface. The imaginary component of InSb’s dielectric function is low throughout the THz range, resulting in a long propagation length for the SP.
Figure 4.3: (a) The measured change in wavenumber (symbols) of an SP on an InSb substrate induced by various thicknesses of polystyrene. Solid lines indicate the results of analytical modelling. The dispersion shift increases rapidly as the excitation frequency approaches the surface plasma frequency (at 1.7 THz). Measurement bandwidth is limited to 1.2 THz by the propagation length of the SP. (b) Equivalent results for a gold substrate. Dashed lines are the results of finite element modelling of the system that includes the effects of input and output coupling blade apertures. (c) Analytical modelling for the gold substrate underestimates the change in dispersion by almost an order of magnitude.
4.4.1 Sample preparation

InSb substrates are prepared by cleaving mono-crystalline wafers in to strips with dimensions 2cm x 3cm. These strips are mounted on glass slides for support and then spin coated with polystyrene.

In the spin coating process the polystyrene is deposited in a viscous solution of methoxybenzene (20% polystyrene by volume) and then spun to form a homogeneous layer on the InSb surface. This is followed by baking at 60 °C to remove the methoxybenzene solvent. The thickness of the polystyrene is controlled by the rotation rate during the spinning stage; using this method we can produce layers of controlled thicknesses between 500nm and around 2 μm, having surface thickness variation away from the edges of less than 50nm. Owing to the high viscosity polystyrene used, edge defects near the sides of the InSb strips are substantial, and the outer 2mm of the InSb wafer has large surface defects in polystyrene films - this region of the samples is not used in experiments. After coating the layer thickness is measured using a mechanical surface profiler.

4.5 Measuring surface plasmon propagation

We determine the dispersion of the surface modes using the THz time-domain spectrometer (with bandwidth of 0.2 - 2 THz) described in Chapter 2, flushed with dry air to minimise absorption of the THz radiation by water. A schematic of the measurement geometry is shown as 4.2. In our experiment we couple to the surface modes on the coated gold and InSb substrates by scattering a focused TM-polarised THz pulse through a 300 μm wide slit aperture formed between the InSb surface and a steel blade. Using a second blade aperture placed 1 cm along the surface from
the input coupling blade, we couple the surface mode back to freely propagating radiation, which is then measured in the far field. This coupling scheme relies on the broad spread of wave-vectors emitted from the wavelength-scale input coupling aperture; some of the wave-vectors will match that of the surface plasmon mode. Similarly the scattering of the SP at the output coupling aperture should produce a wide cone of free-space light which can be gathered for detection.

4.5.1 Analysis

Time-domain electric field profiles of transmitted THz pulses are converted, by means of a Fast Fourier Transform, to complex transmission spectra, \( A(\omega)e^{i\phi(\omega)} \), containing both the amplitude \( A \) and phase \( \phi \) of each frequency component. Normalising these transmission spectra against a reference spectrum (i.e. of a substrate without dielectric layer) yields the analyte-induced change in phase across the sample, \( \Delta \phi \). This corresponds to a change in wavenumber given by \( \Delta k = \Delta \phi / l \), where \( l \) is the propagation length between the blades.

4.5.2 Propagation experiment

The size of phase shift measured is determined by the distance which the SP propagates through the analyte, whilst the upper limit of the measurable frequency range is determined by the propagation length of the SP upon approaching \( \omega_{SP} \). The input/output coupling blades (as well as the associated focal points of the parabolic mirrors) are mounted such that the distance between the blades is variable, controlled by a micrometer translation stage. The distance between the two blades determines the terahertz signal intensity measured at the detection crystal through
two mechanisms. Firstly, the surface plasmon decreases in intensity as it propagates along the surface, with the propagation length being reduced upon approaching the surface plasmon frequency (see Chapter 1). This effect determines the upper frequency limit of the measurement. Secondly, there is a decrease in collection efficiency with increasing propagation length due to the lateral spread of radiation from the input coupling aperture, owing to the conical shape of the focused THz beam at the input coupling aperture. A propagation length of 1.0 cm is chosen through preliminary testing, in which we find that for this distance the size of phase shift at frequencies below the upper limit is measurable for the thinnest polymer films, whilst simultaneously ensuring that the upper limit is well in to the THz frequency range. We find that for a propagation length of 2.0 cm the upper frequency for which we can detect the phase-shift induced by a 500 nm polystyrene film is at 0.9 THz, whilst at 1.0 cm this extended to 1.2 THz. At shorter distances (0.5 cm) the size of the phase shift is reduced linearly, compromising measurement accuracy at lower frequencies.

In Fig. 4.3 the data points represent $\Delta k$ measured for several thicknesses of polymer layer on InSb (4.3(a)) and gold (4.3(b)) substrates, respectively. Firstly, as expected, the phase shifts are larger for thicker polymer films. The measured wavenumber shifts for polymer covered InSb substrates are clearly larger than for the gold substrates. Furthermore, for the InSb samples we can see a clear trend with $\Delta k$ increasing considerably on approaching the surface plasma frequency of the InSb. At 1.2 THz $\Delta k$ is typically twice as large as those for a similar polymer film on the gold substrate.
4.6 Analytical model

It is possible to determine the wavenumber of the SP mode for a three-layer system\textsuperscript{117} (such as our conductor-dielectric-air surface) analytically, through the solution of the expression found as Eqn. 12 of Ref.\textsuperscript{55}:

\[
\tanh(\alpha_2 d) = -\frac{\varepsilon_2 \alpha_2 (\varepsilon_1 \alpha_3 + \varepsilon_3 \alpha_1)}{\varepsilon_1 \varepsilon_3 \alpha_2^2 + \varepsilon_2^2 \alpha_1 \alpha_3} \quad (4.2a)
\]

in which the propagation constants in the three media are \(\alpha_1\), \(\alpha_2\) and \(\alpha_3\):

\[
\alpha_i = k_{sp}^2 - k_0^2 \varepsilon_i, \quad i = 1, 2, 3 \quad (4.2b)
\]

The permittivities \(\varepsilon_{1,2,3}\) refer to the permittivity of the semi-infinite conductor \((\varepsilon_1)\), the dielectric \((\varepsilon_2)\) of thickness \(d\) and the semi-infinite vacuum \((\varepsilon_3)\) above the surface, as indicated in Fig. 4.4. Expressions solving Eqn. 4.2 explicitly for \(k_{sp}(\omega)\) on an asymmetric three-layer surface can be made for the case of very thin films\textsuperscript{26}, however as we need to find the response of a variety of film thicknesses a numerical solution
is more appropriate. Taking Eqn. 4.2 we find the surface plasmon wavenumber \(k_{sp}\), taking the Drude model for the permittivity of the conductor and using a minimisation routine (as in section 3.8) to find a numerical result for \(k_{sp}(\omega)\). We then normalize the wavenumber in the same manner as the experiment, i.e. we find \(\Delta k = k_{\text{poly}} - k_{\text{air}}\), where \(k_{\text{air}}\) is the wavenumber of a SP on an uncoated substrate, and \(k_{\text{poly}}\) the wavenumber with a dielectric coating.

### 4.6.1 Fitting

The best fits as determined by a minimization of the least squares errors between experiment and analytical solution are plotted as solid lines in Fig 4.3(a). Fits are restricted to polystyrene permittivities in the range \(2.5 \leq \varepsilon_p \leq 3.5\). For InSb substrates, the calculated and measured wavenumber changes agree fairly well with a dielectric constant of the polystyrene layer of \(\varepsilon_p = 2.9 \pm 0.02\). The maximum deviation between experimental results and the fits is \(35 \text{ m}^{-1}\), on the 4 \(\mu\text{m}\) film at 1.2 THz. By analyzing the spectral amplitude of the experimental signal with the loss predicted by the analytical model, we ascertain that, for this material, the imaginary component of \(\varepsilon_p\) is negligible \((< 0.1)\) in the THz frequency range.

**Transmission measurements**

The value of \(\varepsilon_p\) and the absence of absorption found from the fits to \(\Delta k\) agree with the results of direct THz transmission measurements on 2 mm thick samples of polystyrene. In these transmission measurements, thick layers of polystyrene are drop-cast on to substrate of fused silica from a 50\%-by-volume solution of methoxybenzene. The solvent is removed in the same manner as for the spin-coated layers.
We measure transmission and directly extract the complex dielectric function of the polystyrene from the Fresnel equations, using the phase information from the terahertz spectra in conjunction with the change in amplitude to yield both the real and imaginary components to the permittivity. These yield a permittivity of $2.92 + 0.1i$ at 1.2 THz, in good agreement with the measurements with the fits to surface plasmon propagation. The marginal increase in the imaginary component to the permittivity of the polystyrene seen in the transmission measurements can be attributed to the change in the preparation process between the drop-cast thick layers and the spin coated thin layers. In the thicker layers the drying of the methoxybenzene solvent is slow, and can lead to trapping of residual solvent inside the polystyrene layer; the solvent impurities will lead to increased terahertz absorption.

### 4.6.2 Fitting with a gold substrate

The results of the analytical model for polystyrene layers on gold substrates are plotted in Fig. 4.3(c); the calculated shifts are more than an order of magnitude smaller than those found for the InSb substrate in Fig. 4.3(a). This highlights the greater sensitivity to dielectric analyte expected for a SP on InSb compared to the surface eigenmode on gold. However, it should be noted that the shifts in wavenumber that we find from our measurements on gold (Fig 4.3(b)) are considerably larger than those predicted by the analytical model (Fig. 4.3(c)). This suggests that, for the gold substrates, we do not experimentally interrogate the eigenmode of the system. Indeed, this is clear when we consider the length scales involved in the experiment: since the electric field of the eigenmode is expected to decay over several centimeters in the direction normal to the surface, we will not excite the gold surface eigenmode.
over the finite lateral propagation length (1 cm) from our small coupling aperture (300 µm). Contrary to previous claims\textsuperscript{44}, the THz aperture coupling technique as presented here and elsewhere\textsuperscript{118} will not, therefore, interrogate the surface plasmon mode of a planar metal surface. Instead, the measurement will be very sensitive to the phase of the diffracted field from our input-coupling aperture.

### 4.7 Finite element model

In order to properly simulate the complete measurement system including the coupling elements, we carry out a full finite element method numerical model using HFSS\textsuperscript{3} (see section 1.6). In order to reduce computational overheads the model is approximated to be semi-infinite in the plane orthogonal to the propagation direction (i.e. in to the plane of the page of Fig. 4.2) by imposing perfect-H boundaries on both sides, giving a repeated section 15 µm in thickness. The sharpened coupling blades are approximated by a thin (40 µm) bar of perfectly-conducting metal placed 300 µm above the surface. The gold surface is represented by a bulk conductivity of $40 \times 10^6$ Sm\textsuperscript{-1}. Phase of the terahertz electric field is calculated at a single point 500 µm above the surface and 500 µm beyond the output coupling aperture in the direction of propagation. A mesh operation restricting the size of tetrahedra in the finite element model is placed around the output coupling aperture and the point of phase-calculation; this increases the model accuracy by ensuring that sufficient computational time is devoted to calculating fields in this region despite the relatively low field intensity owing to the decay of the surface plasmon intensity over the 1cm of propagation.

Whilst computationally demanding, the results of the numerical model (dashed
lines in Fig. 4.3(b)) are much closer to our measured gold data than the analytical solution. The largest deviation between model and experiment is of size \(65\, \text{m}^{-1}\). We find that the numerical model is very sensitive to the precise size and shape of the coupling apertures; we therefore attribute the remaining discrepancies between the numerical model and data to the limited precision with which the experimental configuration can be reproduced in our computer model. On the other hand, analytical modelling is clearly adequate to reproduce the measured phase-shifts induced in the surface eigenmode on an InSb substrate. For these substrates, the confinement of SP electric field on InSb (decay length\(^{26}\) of \(178\, \mu\text{m}\) at 1.2 THz) means that the scattered radiation from the input coupling aperture can efficiently couple to the surface eigenmode well within the 1 cm propagation distance of our experiment.

### 4.8 Lossy analytes

The aperture coupling technique that we employ here allows the interrogation of THz optical properties over a broad frequency range using a simple analytical formula for evaluation. By combining both amplitude and phase measurements, a complete characterization of the optical properties of other analytes, such as those of interest in biological or chemical studies, is therefore possible. Biological analytes, which typically contain water and other polar molecules, are generally characterized by THz dielectric functions with a large imaginary component (for example, the imaginary component of the permittivity of bulk water\(^{119}\) at 1 THz is approximately 9.80). Using our analytical model, we can evaluate the effects of an absorbing analyte, by finding the wavenumber and propagation length for a 500nm analyte layer with dielectric function \(\varepsilon_p = 2.9 + 5i\) - a permittivity which might be typical for a
**Figure 4.5:** (a) Calculated shift in wavenumber caused by a non-absorbing (black two-dash line) and absorbing (red three-dash line) dielectric layer on InSb. (b) Calculated propagation length of SPs propagating on InSb coated with an absorbing dielectric (red three-dash line), non-absorbing dielectric analyte (black two-dash line) and with no dielectric overlayer (blue one-dash line).
mixed-material analyte. In Fig. 4.5(a) we see that the lossy analyte induces only a slight increase in the wavenumber shift above that for a non-absorbing analyte. More interestingly, an absorbing dielectric layer will lead to a significant drop in the propagation length of the SP, which is shown in Fig. 4.5(b). In the figure we plot, on a log scale, the propagation length $\delta_{sp}$ (calculated as in section 1.3.1) as a function of frequency. The drop in propagation length is calculated to be between 15% (at 0.4 THz) and 28% (at 1.2 THz), with a mean drop of 22% in the same frequency range. The drop in propagation length increases approaching the surface plasma frequency of InSb. An absorbing analyte will therefore be more readily identified (and in smaller volumes) than a non-absorbing analyte; further calculations indicate that a film of absorbing analyte as thin as 50 nm will induce a change in propagation length of 4.8% at 1.2 THz. This change is readily measurable in a terahertz spectrometer, which can measure the propagated electric field amplitude with accuracy of greater than 0.001 % as detailed in Chapter 2.

4.9 Conclusions

In conclusion, our results demonstrate that it is possible to use semiconductor surface plasmons to interrogate the THz optical properties of thin film analytes. We show that it is possible to measure the dielectric properties of low index films of thickness almost three orders of magnitude smaller than the wavelength of freely propagating radiation. We show that, by combining the amplitude and phase information in a measurement, the complete dielectric response of such a thin film can be extracted from simple analytical formulations.
Chapter 5

Arrays of subwavelength holes

Summary

In this chapter we measure the enhanced transmission of Terahertz radiation through a metal film perforated with arrays of subwavelength holes of varying hole size. By measuring transmission spectra in the time-domain, and comparing our experimental results to a rigorous modal-matching model, we are able to assess the relative contributions of resonant and non-resonant transmission channels. We see that the contribution of the resonant transmission becomes more important with decreasing hole size, because the lifetime of the surface mode mediating the transmission is increased with reducing hole size. Using low-temperature measurements to control the non-radiative loss-levels in our system, we show that losses limit the lifetime of the surface mode, thereby limiting the resonant transmission intensity for the smallest holes.

5.1 Background

Recent interest in the enhanced optical transmission through arrays of subwavelength holes in metal films was sparked by the seminal work\(^{60}\) of Ebbesen et al., who observed that for appropriate array lattice periodicities and wavelengths the transmission through an array of subwavelength holes can vastly exceed that ex-
expected from the open surface area of the holes. Transmission peaks are typically found at wavelengths close to the lattice periodicity. Since this visible-frequency observation of enhanced optical transmission through hole arrays, the same effect has been seen at infrared\textsuperscript{120}, terahertz\textsuperscript{121} and microwave frequencies\textsuperscript{69} with applications suggested in designing filters\textsuperscript{122}, optical sensors\textsuperscript{123}, microwave devices\textsuperscript{69} and THz optical components\textsuperscript{124}. Since the first experimental observations of this effect, multiple explanatory theoretical models have been developed\textsuperscript{61–63}. It is generally accepted that surface modes (surface plasmons at optical frequencies) play a crucial role. In this respect, a model offering considerable physical insight into the transmission mechanism has been the ‘Fano-type’ mechanism\textsuperscript{125}; in this picture, transmission is interpreted in terms of the interference between two transmission channels: one non-resonant (direct) channel describes transmission through individual, uncoupled holes whilst the resonant channel describes light which traverses the grating through adjacent holes via diffractive coupling to surface modes (see Fig. 5.1). Within this model, one can understand the origin of peaks in the transmission spectra of the hole-arrays in terms of constructive interference conditions, reached when the wavelength of the light is approximately equal to the spacing of the hole-array lattice. Similarly, destructive interference conditions can cause transmission minima. Separating\textsuperscript{66} these transmission channels experimentally can help in determining the qualitative effects of factors such as the material properties\textsuperscript{120}, losses\textsuperscript{126}, structural parameters\textsuperscript{127} and experimental constraints\textsuperscript{68}.

Temporally resolved measurements can help separate the two interference pathways\textsuperscript{128}. Fully time-resolved measurements of the electric field profile of transmitted THz pulses to show that the resonant and non-resonant transmission of the hole arrays can be considered as two distinct, separable phenomena. The system
Chapter 5: Arrays of subwavelength holes

5.1 Background

Figure 5.1: Transmission of a pulse through a hole array. The holes are perforated in a gold film, supported on a substrate of silicon. Time-domain transmission spectra (of the type shown either side of the sample) are measured using a collimated, 1cm diameter beam of THz radiation. The incident vacuum region (1), hole array layer (2) and dielectric substrate (3) are indicated.
we consider is of a hole array in a thin film of conductor, bounded by a dielectric substrate and vacuum superstrate. By measuring and modelling the time-domain transmission of a THz pulse through this hole-array we can recognise how the hole size effects the lifetime of the surface mode mediating the resonant transmission and independently monitor changes in the level of non-resonant transmission with hole size. Similarly to previous work on a triangular lattices of round holes by Miyamaru et. al., we observe that the relative contribution of the resonant transmission becomes larger as the hole size is decreased - due to the corresponding increase of the surface mode lifetime. Using low-temperature measurements, we show how material losses in the system change the surface mode propagation length, and demonstrate how this lowers the transmission and broadens transmission resonances.

5.2 Modal matching model

The transmission through subwavelength hole arrays and related structures in metals at low frequencies (such as the THz range and below) has been successfully modeled using modal-matching techniques, which are well suited to the problem since the boundary conditions are easily defined.

The physical system we consider is a thin film of conductor perforated with a two-dimensional square lattice (pitch $d$) of small square-sided holes (side $a$) - indicated in Fig. 5.1. The conductor is supported on a dielectric substrate (permittivity $\varepsilon_s$), with the superstrate being vacuum with refractive index of unity. In our modal-matching model the electromagnetic fields in the superstrate and substrate are matched to the fields in the waveguide modes of the subwavelength holes; by exploiting the continuity of electric and magnetic field at the boundaries of the interfaces we can
obtain explicit analytical expressions for transmission and reflection of our thin hole array. The formalism of this model is included as Appendix A, which is established along the same principles as the earlier work of Mary et al.\textsuperscript{72}

In Fig. 5.2(a) we show calculated transmission spectra for a system consisting of a hole array with lattice pitch of 100 \( \mu \text{m} \) perforated in a perfect conductor on a loss-less substrate of silicon, described by \( \varepsilon_s = 11.85 \). The hole size varies from 25 \( \mu \text{m} \) to 85 \( \mu \text{m} \) as indicated in the figure legend. Calculated transmission through the holes is normalised against the transmission through a plain silicon-air interface, in order to compare it to experimental results. In the frequency domain spectra we can see two peaks within the range plotted, one at 0.86 THz and another at 1.22 THz. Both resonances have the characteristic asymmetric ‘Fano’ type shape\textsuperscript{131}.

In the ‘Fano-type’ picture for hole array transmission\textsuperscript{125} we consider that there are two paths for light incident on the array to be transmitted by the structure. Firstly there is the non-resonant transmission, in which light couples in to and out of the zero-order waveguide mode inside the holes. The second method is surface-mode mediated resonant transmission; for this path light incident on the hole array is coupled, via the array periodicity, to surface mode propagating on the interface between the conductor and the dielectric. The combination of constructive and destructive interference between these two mechanisms gives the aforementioned characteristic resonance shape. A schematic of these two pathways is shown as part of Fig. 5.1

The approximate resonant frequency of each transmission maximum (\( \nu_r \)) can be found from the equation\textsuperscript{125}:

\[
\nu_r = \frac{\omega_r}{2\pi} = \frac{c\sqrt{l^2 + j^2}}{d\sqrt{\varepsilon_d}},
\]

(5.1)
in which the resonance position is determined by the lattice periodicity $d$, and the
permittivity of the dielectric above the conductor, $\varepsilon_d$. The mode indices $i$ and $j$
are integers indicating the direction of the surface mode propagation across the
hole-array lattice. This equation is an approximation made for the case of a lattice
of infinitesimally small holes perforated in a thin sheet of perfect conductor; the
introduction of finite hole size causes slight shifts in the resonance position\textsuperscript{68}. From
equation 5.1 we can surmise that the two resonance peaks seen in the transmission
spectrum of Fig. 5.2(a) are due to a surface mode on the silicon-gold interface; with
the modes corresponding to the $< 1, 0 >$ and $< 1, 1 >$ directions across the hole
lattice, as indicated on Fig. 5.2(a). Equivalent resonances arising from the surface
mode on the gold-air interface will lie beyond $\approx 3 \text{ THz}$.

In Fig. 5.2(a) it is interesting to note that the maximum value of transmittance
for the $< 1, 0 >$ resonance is the same for all hole sizes, and equal to the transmit-
tance of the plain silicon interface (i.e. on resonance the normalised transmission
in Fig. 5.2(a) is 1.0). On decreasing the hole size, the resonance width decreases,
tending to an infinitely narrow resonance for infinitely small holes. Note that this
behaviour is not observed for the $< 1, 1 >$ and higher order resonances, since at
frequencies above 0.86 THz some power is radiated through higher diffracted orders
(other than the zero-order mode).

### 5.3 Time-domain response

This behaviour can be understood more clearly if we turn to the time-domain re-
response of the system. We can evaluate the temporal dependence of the transmitted
fields $E(t)$ through the inverse Fourier transform

\[
\text{Chapter 5: Arrays of subwavelength holes} \quad 5.3 \text{ Time-domain response}
\]
\[
E(t) = \int_0^\infty t^{0,0}(\omega)E_{in}(\omega)e^{i\omega t}dt,
\]

where \(E_{in}(\omega)\) describes the incident field. For this incident field we apply the experimentally measured spectrum of a broadband pulse from a THz spectrometer (shown as the incident pulse in Fig. 5.1. The resulting time-domain electric field profiles are shown as Fig. 5.2(b)). In this figure we can see two distinct regions to the time-domain transmission plot. The initial non-resonant transmission pulse (indicated as pulse ‘A’) corresponds to the radiation that has been transmitted straight through the holes without coupling to a surface mode. The second region (pulse-train ‘B’) corresponds to radiation that has coupled to the surface mode before being transmitted. In the time-domain traces the field amplitudes are scaled such that the peak field of the non-resonant pulse is the same for all hole sizes; this allows us to compare the relative change in field amplitude between the resonant and non-resonant sections of the time-domain traces. Scaling factors are indicated in the figure legend.

We can now consider in more detail the resonant transmission pulses in region (B) of Fig. 5.2(b). In the time-domain traces the amplitude of the resonance oscillations decreases over time; for the smallest holes this decay-time is longer. The lifetime of these resonance pulses in region ‘B’ determines the width of the transmission resonances in Fig. 5.2(a) - longer lifetime corresponds to a narrower resonance in the frequency domain. The pulses of region ‘B’ are shown extended to 200 picoseconds in Fig. 5.3, in which the decay rate of all the pulse trains can be clearly seen. Note that there is very little decay in the amplitude of the resonance oscillations for the 25 \(\mu\)m holes even after an interval of 50ps. The decay time in this idealised model is determined purely by phase-retardation across the width of the
Figure 5.2: Calculated transmission spectra through a 100μm pitch hole array in a thin conducting film shown in the frequency domain (a) and in the time domain (b). In the time domain, regions of non-resonant transmission (A) and surface-mode-mediated transmission (B) are indicated. The time-domain traces are scaled to facilitate comparison between the pulse amplitudes, scaling factors $f$ are indicated; the plotted field is $E_{\text{trans}}/f$ for each trace.
Chapter 5: Arrays of subwavelength holes  

5.3 Time-domain response

Figure 5.3: Extension of the same time-domain traces shown in Fig. 5.2(b) to 50 picoseconds. The increase in the lifetime of the resonant modes with decreasing hole size can be clearly seen.

holes; larger holes have a wider resonance as the phase-shift across the hole width is larger.

Here we should also note that as well as a change in the resonant oscillation decay time there is also a change in the shape of the waveform in region ‘B’ as the hole size is reduced. This is due to the relative intensities of the $<1,0>$ and $<1,1>$ modes (both of which are present in the pulse train) changing as a function of hole size, as can be seen in the frequency-domain spectra of Fig. 5.2(a); such effects have been observed previously as an effect of the hole shape$^{70}$.  

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From this time-domain analysis of the transmission spectra we have seen evidence for the underlying mechanisms and the factors determining the resonance width. We shall now move on to consider equivalent time-domain spectra from experimental measurements.

5.4 Experimental measurements

Previous measurements in the THz frequency range\textsuperscript{68,132} have been made on hole arrays formed from thin perforated metal films on dielectric substrates. In the THz frequency range it is possible to exploit techniques of THz generation and detection coupled to ultrafast laser sources in order to extract extra information about the hole array transmission; for example by using an optical pulse as a near-field probe of THz radiation\textsuperscript{133}, or by using an amplified laser pulse to dynamically modify the properties of the structure\textsuperscript{134}.

5.4.1 Samples

Our samples consist of a 150 nm thick layer of perforated gold film on top of a doped silicon wafer substrate with thickness 500 $\mu$m; the hole-arrays are fabricated by contact lithography, followed by the evaporation of the gold film and a lift-off process to form the array of holes. Each hole array sample covers a square area of side 2.5 cm, with all the arrays on a single 15 cm diameter wafer. An area of the wafer is left uncoated (plain silicon) for use as a reference.
Chapter 5: Arrays of subwavelength holes  5.4 Experimental measurements

Figure 5.4: Transmission spectra through hole arrays with hole sizes varying from 25 to 85 μm. (a) Experimental frequency-domain transmission spectra. (b) Experimental time-domain spectra. Scaling factors (f) are indicated, such that the plotted field is $E_{\text{trans}}/f$.  

(a) Measured transmission

<table>
<thead>
<tr>
<th>Hole sizes</th>
<th>Transmitted intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 μm</td>
<td></td>
</tr>
<tr>
<td>35 μm</td>
<td></td>
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<tr>
<td>45 μm</td>
<td></td>
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<td>55 μm</td>
<td></td>
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<tr>
<td>65 μm</td>
<td></td>
</tr>
<tr>
<td>75 μm</td>
<td></td>
</tr>
<tr>
<td>85 μm</td>
<td></td>
</tr>
</tbody>
</table>

(b) Measured transmission

<table>
<thead>
<tr>
<th>Hole sizes</th>
<th>Electric field (arbitrary, scaled)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 μm</td>
<td></td>
</tr>
<tr>
<td>35 μm</td>
<td></td>
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<tr>
<td>45 μm</td>
<td></td>
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<td>65 μm</td>
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<tr>
<td>75 μm</td>
<td></td>
</tr>
<tr>
<td>85 μm</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.5: (a) Spectra through the hole arrays, calculated using the modal matching model, with the incorporation of loss in the silicon layer. (b) Calculated time-domain spectra, taken from the IFFT of the calculated spectra. Scaling factors ($f$) are indicated, such that the plotted field is $E_{\text{trans}}/f$. 

Chapter 5: Arrays of subwavelength holes

5.4 Experimental measurements
5.4.2 Transmission spectra

We measure the zero-order transmission of the hole arrays using a time domain THz spectrometer, as described in Chapter 2. The incident THz pulses are essentially single cycle electromagnetic pulses (see the incident pulse of Fig. 5.1) of about 1 ps duration and peak field strength approximately 1 kV/cm when focused for detection. The time-dependent electric field profile is detected directly in the far-field. The spectrometer is flushed with dry air to prevent absorption by water vapour. By taking the discrete Fourier transform of the time-domain waveforms we obtain the frequency domain spectrum $E(\omega)$. From this we obtain intensity transmission spectra, $T(\omega) = |E_t(\omega)|^2/|E_s(\omega)|^2$, i.e. the field transmitted through the hole array $E_t(\omega)$ is normalised by the field transmitted through the substrate alone, $E_s(\omega)$. The spectral resolution of the resulting frequency domain trace is determined by the time-window over which we measure the corresponding electric field profile; our maximum time-domain scan length is limited by reflections within the silicon wafer. Note that we measure with a large area (1 cm diameter), collimated beam in order to avoid limitations found in previous measurements due to finite beam size and angular resolution. We also use large-area samples (2.5 cm sided squares) to minimise the effects of finite sample size and ensure that our results comparable to the infinite array of our analytical model. We estimate that our 1 cm diameter THz beam will allow a coherent measurement window of around 30 ps, significantly larger than that imposed by the multiple reflections within the silicon substrate (around 10 ps).

In Fig 5.4(a) we show experimentally measured frequency-domain transmission spectra through the hole arrays, normalised by the transmission through the silicon
substrate. The spectral resolution of all these traces is 66 GHz, determined by the 
15 ps scan duration of the time-domain measurements. As in the model of Fig. 
5.2(a) there are two distinct resonance peaks for all hole sizes, at approximately 
0.86 THz and 1.22 THz. The smaller oscillations throughout the frequency domain 
spectra are caused by taking the Fourier transform of the random instrumental noise 
present from our time-domain traces over a finite time-window.

There are clear differences between these measured traces and the modelled 
data shown in Fig 5.2(a). In the frequency-domain we see that as the hole size 
is reduced, the peak transmission amplitude decreases, in contrast to the simulated 
data of Fig. 5.2(a) in which the peak amplitude is 1.0 for all hole sizes. Furthermore 
the transmission width in the experimental spectra does not narrow continuously 
with hole size, and the smaller hole size resonance peaks are considerably broader 
than those in Fig. 5.2(a).

We can once again obtain a clearer picture of the transmission behaviour by 
looking at the time-domain spectra, which show the origins of this discrepancy. In 
Fig. 5.4(b) we show the original time-domain traces used to calculate the measured 
transmission spectra. The train of pulses corresponding to the resonant transmission 
decays in amplitude more rapidly than in the model of Fig. 5.2(b). This effect is 
particularly evident in the smallest holes - for the 25µm holes we see an appreciable 
decay in the measured time-domain spectra whereas there is very little temporal 
decay in amplitude for the pulse-train in the model of Fig. 5.2(b). Clearly, the 
lifetime of the measured surface mode is lower than in Fig. 5.2(b), and this is 
limiting the transmission magnitude.
5.4.3 Effects of losses

The disparity in surface mode lifetimes between Figs. 5.2(b) and 5.4(b) is caused by losses in the silicon substrate of our system, which has a non-zero imaginary component to its dielectric function. At THz frequencies, we are highly sensitive to absorption caused by free carriers introduced to the silicon crystal by the presence of impurities. Such free carriers can contribute to absorption even at relatively low concentrations. We can measure the free-carrier concentration and indeed the full complex dielectric function of the doped silicon wafers using transmission measurements, following the methodology of Jeon et al. We find a frequency variant complex dielectric function to our silicon as shown in Fig. 5.6, ranging between 0.5 and 1.5 in the frequency range of interest; this corresponds to a DC conductivity of approximately 32 Ω m$^{-1}$. Adding this lossy dielectric function to our analytical model yields the plots of Fig. 5.5(a). In these plots the addition of loss quenches the propagation of the resonant surface mode; the resonances are both lower in amplitude and broader in width. In the time-domain (Fig. 5.5(b)), the resonant transmission pulses decay more rapidly after the initial pulse, corresponding to a reduced propagation length for the surface mode. The addition of loss to the modal-matching model produces results which closely match the experimental spectra in both the time-domain and frequency domain. The remaining discrepancy between the modelled and experimentally measured transmission is in the absolute transmission magnitude across the spectrum, which is slightly lower in the measured spectra of Fig. 5.4(a) than in the modelled spectra of Fig. 5.5(a). This is due to the propagation of the pulse through the 500 μm thick lossy silicon substrate; this propagation distance is not accounted for in the calculated transmission spectra.
From these results we can infer that losses play a crucial role in determining the transmission, especially in the smallest holes for which hole-array surface-mode lifetime is the longest.

5.5 Temperature dependence of transmission

We have identified a transmission mechanism for our sample in the time-domain spectra, and shown the effects of surface-mode lifetime in determining the transmission characteristics. In this section, we demonstrate control over the surface mode lifetime through variation of the temperature of the silicon substrate; by cooling the substrate we are able to trap the impurity carriers and lower the lossy component of the silicon dielectric function. Such thermal control over the semiconductor dielectric function can give extra insight in to the transmission mechanism through the hole arrays.
5.5.1 Sample cooling

Thermal control is accomplished by cooling the hole-array sample in a continuous-flow liquid-Helium cryostat; the sample is mounted in close thermal contact with a copper cold-finger inside which liquid helium is constantly circulated. The cryostat is fitted with a calibrated thermocouple temperature probe and a heating element; combining this with a digital thermostat controller we can maintain the temperature of the cold-finger within 0.001K at 4.2K, and to within 0.1K at 292K. The sample is contained within a vacuum chamber with quartz windows allowing us to take THz transmission spectra in the same manner as for previous samples. Such cooling will reduce the number of free charge carriers by orders of magnitude\(^*\), lowering the loss levels in the substrate to near-negligible levels. In Fig. 5.6 we show the imaginary component to the permittivity of the silicon measured at 4.2K, which has decreased by a factor of around four from the room temperature values; the small residual imaginary component is due to scattering by defects in the silicon crystal structure. By cooling to this level, we will begin to approach the model of Fig. 5.2 in which the silicon substrate has no imaginary component to its permittivity.

It should be noted that the introduction of the cryostat places some extra constraints on the experimental system; the two quartz windows reduce the terahertz transmission by a factor of 1.8, and vibration from the liquid helium pump adds some extra experimental noise.

\(^*\)At 4K, well below the donor ionisation energies, it is possible to perform a simple calculation\(^{\text{34}}\) from Kittel chapter 8, of the carrier concentration \((n)\) in the silicon using the formula

\[
\frac{n}{n_0} = 2(\frac{m_e}{\pi \hbar^2})^{3/2} \exp\left(-\frac{E_d}{k_B T}\right),
\]

dependent on the impurity concentration \(N_d\), ionisation energy of the impurities \(E_d\) and \(n_0 = 2(m_e k_B T/2\pi \hbar)^{3/2}\). Using a simple Drude fit of our complex permittivity in Fig. 5.6, we estimate that the charge carrier concentration in the silicon is approximately \(10^{21}\, \text{m}^{-1}\) at room temperature; the temperature dependence indicates that this concentration should decrease to nearly nil at 4.2K.
5.5.2 Low temperature transmission spectra

In Fig. 5.7(a) we plot measured time-domain traces through holes of size 55 \( \mu m \) at both room temperature (292 Kelvin) and at 4.2 Kelvin. From the time domain traces we can see a distinct difference in the lifetime of the resonance oscillations between the trace at low temperature (blue) and at high temperature (red). In this plot the two traces are scaled to the same peak electric field amplitude in order that we can directly compare the decay rates of the resonance oscillations.

If we compare the change in the peak oscillation amplitude between 8.80 ps and 14.45 ps for both the hot and cold time-domain traces, we find that at 4.2K the peak electric field amplitude has decayed to \( 0.37 \pm 0.1 \) of its initial value. Over the same time interval in the 292K trace the field has decayed to \( 0.33 \pm 0.1 \) of its initial value. This comparison between pulse peak field amplitudes indicates that when we decrease the loss in the substrate by cooling the silicon, the surface mode lifetime is increased.

For a more thorough characterisation of the surface mode lifetime, we can use a numerical fit to the data, shown as Fig. 5.7(b). The goal of this fitting procedure is to directly compare the lifetime of the surface modes mediating this transmission when we change the temperature of the sample. In the numerical fit we treat the decay of the resonant transmission oscillations in Fig. 5.7(a) as Lorentzian (i.e. exponential in form). We fit the resonant oscillations of the time-domain traces to the equation

\[
E(t) = A_{1,0}\sin(\omega_{1,0}(t - t_{s,1,0}))e^{-t/\tau_{1,0}},
\]

essentially an exponentially decaying sinusoidal function. The quantity of interest is the decay time of the predominant \( <1,0> \) resonance, \( \tau_{1,0} \). There will also be a
contribution from the 1,1 resonance - however it is clear from the frequency domain spectra of Fig. 5.2(a) that the $<1,0>$ resonance dominates in the transmission of the 55 $\mu$m holes. Further terms in Eqn. 5.3 are $\omega_{1,0}$ the frequency of the $<1,0>$ transmission peak seen in the frequency-domain spectra (shown as Fig. 5.2(a)). $A_{1,0}$ is the starting amplitude of the oscillations, and the starting time offset is $t_{s:1,0}$.

In the fitting procedure, we first scale the measured time-domain traces at both temperatures so as to have the same peak electric field transmission level in the background pulse; this effectively removes the effect of the radiation propagating through the 500 $\mu$m thick silicon wafer. Disregarding the non-resonant transmission pulse we use a least-squares fitting algorithm to fit Eqn. 5.3 to the resonance oscillations for the 4.2K measurements in the interval from 8.0 ps to 16.0 ps. We point out that it is only because we have time-domain data which allows us to temporally separate the surface mode resonance oscillations from the non-resonant transmission pulse that we can use this technique to directly yield a surface-mode lifetime. From the least-squares fit, we determine the resonance lifetime $\tau_{1,0}$ as well as the free parameters $A_{1,0}$ and $t_{s:1,0}$. The frequency $\omega_{1,0}$ is fixed at the centre frequency of the resonance peak seen in the frequency domain spectra (Fig. 5.2(a)). We then perform the same fit on the room-temperature data, this time constraining $A_{1,0}$ and $t_{s:1,0}$ to be the same as for the data at 4.2K; we are essentially assuming that low and high temperature resonances have the same initial amplitude and phase at the time of excitation. For the room-temperature oscillations we fit only the exponential decay time, $\tau_{1,0}$. Using this method the change in $\tau_{1,0}$ as a function of temperature will be an effective measure of the change in the surface mode lifetime.

In Fig. 5.7(b) we show just the resonance oscillations at 4.2K and 292K alongside the decaying exponential envelope of the $<1,0>$ resonance oscillations, having
Figure 5.7: (a) Time-domain spectra through the 55 µm holes at 292 K and at 4.2 K Electric field amplitudes are scaled to the same peak level. (b) Fitting a Lorentzian form to the resonant component of the data with the surface mode lifetimes indicated. (c) Transmission intensity spectra of the 55 µm holes at 292 K and 4.2 K; the 4.2 K spectrum is scaled to match the peak transmission intensity of the 292 K spectrum in order to compare resonance mode widths.
Chapter 5: Arrays of subwavelength holes 5.5 Temperature dependence of transmission

functional form \( A_{1,0}e^{-t/\tau_{1,0}} \). The parameters \( A \) and \( \tau_{1,0} \) are determined from the fitting procedure above. Additionally in Fig. 5.7(b) we show in grey the section of the time-domain trace corresponding to the non-resonant transmission which we disregarded in the Lorentzian fits.

From the exponential envelope in Fig. 5.7(b) we can see that the lifetime of the surface mode resonance transmission has increased from 4.9±0.2 ps to 5.9±0.2 ps upon cooling the sample. The residual 5.9 ps decay time is mostly due to the phase-retardation across the width of the holes.

In Fig. 5.7(c) we see how this change in surface mode lifetime changes the width of the transmission resonances. In this figure we plot the frequency domain transmission intensity at room temperature and at 4.2K; again normalising by the transmission through a plain silicon interface. In order to compare the mode widths the peak transmission of the 4.2K trace is scaled to the same level as the room temperature spectrum. We can calculate each resonance’s Q-factor, \( Q = \nu_0/\Delta \nu \), where \( \nu_0 \) is frequency of the resonance peak and \( \Delta \nu \) is the full-width at half the maximum intensity. This shows \( Q \) for the \(<1,0>\) increasing from 5.0±0.2 at room temperature to 6.6±0.3 at 4.2K; we can conclude therefore that the change in surface mode lifetime dominates the resonance width.

5.5.3 Limitations on the low-temperature lifetime

For a completely loss-free system, we would expect the resonances in the 55 \( \mu \)m holes to have a Q-factor of 18.1 (from the lossless model of Fig. 5.2(a)), and a lifetime equivalent to that seen in the extended time-domain model of Fig. 5.3. We do not recover this long-lifetime resonance and the associated narrow frequency-domain
mode for several reasons. Firstly, as for the previous measurements, the 66 GHz frequency resolution of the time domain spectrometer (determined by the length of the time-domain scan) imposes a lower limit on the measurable mode width of $Q = 12.1$. Increasing the silicon wafer thickness beyond 500 $\mu$m would extend the maximum length of time-domain scan available before a Fabry-Pérot reflected pulse is detected; up until the point where pulses reflected in the spectrometer optics and the THz generation crystal are reached (see Chapter 2), around 20ps after the initial excitation pulse. The mode lifetime itself, as extracted in Fig. 5.7(b), is likely limited by imperfections and defects in the sample. The measured low-temperature dielectric function of the silicon in Fig. 5.6 indicates that there are some residual losses in the wafer despite the cooling, which will limit the mode lifetime. Imperfections in the lattice structure will lead to inhomogeneous broadening of the resonances. Inspection of the hole arrays under an optical microscope allows us to estimate that the random variation in hole size and position across the array is approximately 0.5 $\mu$m; this estimate is taken by sampling 20 individual holes across the array of 55 $\mu$m holes and measuring them against a calibrated micrometer scale. From the lossless analytical model we can estimate that an increase in hole size of 1 $\mu$m, if applied for every hole across the array, could change the Q-factor of the 55 $\mu$m hole resonance by 10% (e.g. Q changes from 18 to 16 when the hole size is changed from 55 to 56 $\mu$m). Although it is difficult to model truly random variation across a structure, this figure gives an impression of the effects of the inhomogeneous broadening from structural defects.

From these low-temperature measurements we can conclude that there are distinct factors determining the surface mode lifetime (and mode-width of the transmission resonances); one is the intrinsic losses of the materials which constitute the
sample combined with inhomogeneities in the hole array lattice, whilst the other is a dephasing effect determined by the size of the holes in the array. In the complete absence of substrate losses and sample inhomogeneities, for a sample with extremely small hole size, the resonance width will eventually be limited by the losses in the metal layer, i.e. the surface plasmon lifetime. At THz frequencies surface plasmon lifetimes on metals are in excess of 1 ns, from which one can infer a lower limit to the resonance width of less than 0.6 GHz. This gives a Q-factor for such a resonance of $>1000$.

5.6 Conclusions

To conclude, we have measured the enhanced transmission of THz radiation through a metal film perforated with arrays of subwavelength holes with various hole sizes. By measuring in the time-domain and comparing our results to a rigorous modal-matching model, we are able to assess the relative contributions of resonant and non-resonant transmissions channels. We see that as the hole size is decreased, the resonant channel comes to dominate the transmission; it does so as the lifetime of the surface mode mediating the resonant transmission increases concomitantly with decreasing hole size. Conversely the level of non-resonant transmission decreases with decreasing hole size.

Using low-temperature measurements, we are able to separate the surface mode lifetime into the intrinsic lifetime (due to pure dephasing effects determined by the size of the holes) and the lifetime due to losses in the substrate. We find that even modest loss levels have profound effects when measuring transmission through the very smallest holes. With this knowledge we can infer a lower limit for the resonance
width in an array of extremely small holes on a lossless substrate of less than 0.6GHz, determined by the lifetime of a THz surface plasmon on a metal film - essentially the limiting case in which the transmission is almost purely surface-mode mediated. In this limiting case, the Q-factor of the transmission resonance becomes extremely high \( Q > 1000 \), with our model of Fig. 5.2(a) indicating near-unity transmission on resonance for such a structure. We point out that physical constraints such as sample size and homogeneity would probably limit the Q-factor before surface mode losses will. However, the potential for a high Q-factor suggests that such hole arrays hold promise as the basis for a very narrowband filter.
Chapter 6

Photomodulation of hole array
surface modes

Summary

We modulate the transmission of THz radiation through periodic arrays of subwavelength holes in a metallic film by using pulses of visible-wavelength light to photo-excite the semiconducting substrate of the hole arrays. By varying the photo-doping level of the semiconductor we are able to switch off the resonant transmission of THz radiation through the array. By varying the size of the holes, we demonstrate the crucial role that surface modes play in the resonant transmission and ultimately in the photomodulation behavior of these structures.

6.1 Background

Photonic structures which incorporate some degree of dynamic control over their electromagnetic properties\textsuperscript{136,137} are interesting for numerous reasons. Some structures have direct applications in proposed photonic devices; in others the dynamic control can provide direct evidence for transmission pathways and for the role of
material properties in determining the behaviour of a structure\textsuperscript{138}. Manipulating material properties optically\textsuperscript{65,134,139–143} is of particular interest, as changes to the structure can be made on the same time-scale as the transit of light pulses through the system.

One very fundamental photonic structure is an array of subwavelength holes perforated in a conducting screen. Such arrays can exhibit narrow transmission resonances\textsuperscript{60} for wavelengths determined by the periodicity of the array - this is known as Extraordinary Optical Transmission, or EOT. The mechanisms underlying EOT in these arrays have been the subject of considerable debate\textsuperscript{61–63}, however consensus has gradually emerged that for many structures the transmission is mediated at least in part by electromagnetic surface modes at the interface between the perforated conducting screen and the dielectric layers by which it is bound\textsuperscript{125,144}.

\section*{6.2 Approach}

In this chapter we use pulses of visible light to modulate the transmission of THz radiation through periodic arrays of subwavelength holes in a metallic film fabricated at the interface of a substrate of crystalline silicon. By varying the photo-doping level of the silicon we are able to switch off EOT of THz radiation through the array. By varying the size of the holes we are able to explain the photomodulation effects in terms of the properties of the surface mode which mediates the enhanced transmission; in particular we can make a direct link between the lifetime of the surface mode and the magnitude of the photomodulation. We show that if we extend the surface mode lifetime by minimising losses and reducing the hole size it is possible to attain photomodulation levels which are orders of magnitude greater
**Figure 6.1:** (a) Diagram of the experimental measurement. A visible pump pulse with centre wavelength 400nm illuminates an array of holes in a gold film on substrate of silicon. 40 ps after the arrival of the pump pulse, a probe pulse in the THz range is transmitted through the hole array and subsequently detected in the far-field. (b) Side profile of the photoexcited structure, indicating the 100 µm array pitch and hole size \( a \).
than those found for a plain silicon surface.

6.3 Structure

The hole-array structure we shall consider in this work (Fig. 6.1) is formed from a 150 nm thick film of gold on a silicon substrate. The gold is perforated with a square lattice (pitch 100 µm) of square subwavelength holes - the holes have sides ranging in size from 25 to 85 µm. The same hole arrays are used for the work in Chapter 5 where they are described in detail.

6.3.1 EOT resonances

Previous works have shown\textsuperscript{132,134,145,146} that such hole-array structures exhibit EOT at terahertz frequencies. The mechanism underlying the transmission can be considered as a Fano-type picture in which resonances arise from constructive interference between radiation which has transmitted straight through the holes, and radiation which has been transmitted after coupling to a surface mode on the metal-dielectric interface\textsuperscript{125}. The frequencies of the EOT resonances $\nu_r$ are determined by the hole array lattice pitch $d$ and the permittivity of the dielectric substrate, $\varepsilon_d$ and are approximately given by:

$$\nu_r = \frac{\omega_r}{2\pi} \approx \frac{c \sqrt{i^2 + j^2}}{d \sqrt{\varepsilon_d}},$$

(6.1)

where $i$ and $j$ are integers indicating the diffracted order coupling to the surface mode. We determine that the hole arrays under investigation have two EOT resonances in the measured frequency range of 0.4 to 1.4 THz, labeled as the $<1,0>$ and $<1,1>$. Both are due to surface modes on the interface between the silicon
substrate and the gold film (modes on the opposing gold-air interface lie outside the spectral range of the incident terahertz pulse, above 3 THz). In this work we chiefly discuss the lowest-frequency ($< 1, 0 >$) resonance as changes to the relative coupling intensity between the higher order modes are complex and highly dependent on sample geometry\textsuperscript{146}. The amplitudes and widths of the transmission resonances are determined by the lifetime of the surface mode mediating the transmission\textsuperscript{129}. For a hole array made from lossless materials the lifetime of the surface mode is entirely determined by phase-retardation across the width of the holes; i.e. arrays with larger holes exhibit a shorter mode lifetime\textsuperscript{129,146}. Through photoexcitation of the silicon surface in these samples one can effectively control this surface-mode mediated element of the EOT transmission, and alter the amplitude of the EOT resonances\textsuperscript{134}.

### 6.4 Terahertz pump-probe

In Figure 6.1(a) we show a schematic of the optical-pump, terahertz probe scheme which is described in detail in section 2.10. Two pulses (both arriving at a repetition rate of 1.05 kHz) separated by a 40 picosecond optical delay illuminate the hole array structure at the air-gold interface. The first pulse to arrive is the 400 nm pump pulse, which photo-excites the silicon exposed in the holes (Fig. 6.1(b)). These 400 nm pulses are generated through non-linear frequency up-conversion of 800 nm pulses in a BBO crystal\textsuperscript{147}; the beam from the crystal is expanded to a circle of 3 cm diameter to ensure that the region of photoexcitation is homogeneous across the 2 cm square sided sample area. The region of silicon photo-excited is very thin, as the penetration depth of the 400 nm light in the silicon is sub-micron\textsuperscript{148}. The
relaxation time for photo-excited charge carriers in silicon at room-temperature is of the order of microseconds\textsuperscript{149} and so a 40 picosecond interval after the arrival of the pump pulse the silicon is in a steady, fully-photoexcited state i.e. we have essentially formed a thin film of extra charge carriers on the silicon interface underneath the holes. By fitting a Drude response to the measured permittivity of these carriers\textsuperscript{11}, we determine that our most intense photoexcitation beam produces a charge density in the silicon of approximately $2.8 \times 10^{24} \text{ } m^{-1}$, corresponding to a plasma frequency of 30 THz. After the 40 ps interval the THz probe pulse arrives in a 1 cm diameter collimated beam. We detect the terahertz pulse which has transmitted through the sample in the far field using a terahertz spectrometer as described in Chapter 2. In this technique we measure the electric fields of the transmitted terahertz pulses as time-domain spectra\textsuperscript{146}; these can be converted to transmission intensity spectra by taking the Fourier transform of the time domain pulses, squaring the field amplitude and normalising by a reference spectrum.

6.5 Transmission spectra

In Fig. 6.2 we show transmission spectra taken through arrays of 45 \textmu m holes for varying fluence of the 400 nm pump pulses. The two expected resonances ($< 1, 0 >$ and $< 1, 1 >$) are seen in the spectra. As we add an increasing fluence of 400 nm pulses we observe a distinct quenching of transmitted terahertz intensity at resonance. The quenching effect at the resonance peak is much higher than the quenching of the non-resonant transmission (which is dominant at lower frequencies). It can also be seen in Fig. 6.2 the the position of the resonance peaks changes slightly upon photoexcitation - the highest intensity red-shifts the resonance by
Figure 6.2: THz transmission spectra through arrays of 45 µm holes with various fluences of 400 nm pump beam. Photoexcitation quenches the EOT resonances, indicated as the $<1,0>$ and $<1,1>$ peaks.

approximately 10 GHz. Similar shifts have been seen previously as an effect of the hole size; as the photoexcitation beam changes the index of the silicon layer below the holes we can attribute this shifting to an equivalent change in the ‘effective’ hole size upon photoexcitation.

At the $<1,0>$ resonance peak a pump fluence of 0.054 J/m$^2$ reduces the THz intensity by a factor of 0.69 - whereas at 0.6 THz, just below the resonance frequency, transmission intensity reduces by a factor of only 0.88. To compare this level of photo excitation, we can define a photo-modulation ratio, $P$:

$$P = \frac{(I_0 - I_{pm})}{I_0} \quad (6.2)$$

where $I_0$ is the peak THz transmission intensity with no photo-excitation, and $I_{pm}$ is the same peak THz transmission intensity with a given fluence of 400 nm photo-
excitation pulses.

6.6 Modulation levels

We compare these photomodulation levels directly in Fig. 6.3(a). In this figure we plot the photomodulation ratio $P$ at 0.86 THz (the peak of the $<1,0>$ resonance) as a function of the fluence of 400 nm pulses for various hole sizes, as well as for the reference surface of unstructured silicon. We expect the plain silicon surface to exhibit the same amount of photomodulation as the non-resonant component of the hole array transmission, as in both cases radiation transmits through the photo-excited region with wave-vectors perpendicular to the interface. The hole array structures will introduce surface modes to the transmission - these surface modes have wave-vectors parallel to the gold silicon interface. For this reason we expect the transmission resonances to be more strongly modulated than the transmission through the plain silicon interface; this effect can be seen in Fig. 6.3(a) as the traces for the hole arrays all lie above that for the unstructured silicon.

6.6.1 Modulation and hole-size

In Fig. 6.3(b) we plot the modulation as a function of hole-size for various fluences, as well as for the unstructured silicon interface. We see a marked increase in the modulation as we decrease the hole size from 85 to 45 $\mu$m for all fluences, indicating that as we decrease the hole size the surface mode is predominating in the transmission. However, for the very smallest holes, the trend is reversed and the resonant transmission for the 25 and 35 $\mu$m holes is clearly less strongly modulated than for the 45 $\mu$m holes. In a lossless hole array, one might expect that the photomodulation
Chapter 6: Photomodulation of hole array surface modes

6.6 Modulation levels

Figure 6.3: (a) Photomodulation versus fluence of 400 nm pump pulses for three sizes of hole and a reference surface of silicon. (b) Experimentally measured photomodulation vs. hole size for various fluence of 400 nm pump pulses. Note that for the 25 µm holes it was not possible to measure photomodulation for the lowest fluences due to the low level of transmitted THz signal. (c) Numerically modelled photomodulation of the THz transmission at resonance as a function of hole-size at a 400 nm pump fluence of 0.197 J/m², with and without loss in the silicon substrate.
effect would be greatly enhanced for arrays of very small holes, as the lifetime of the surface mode is increased. To see the origins of this effect we must use a finite element mode incorporating the full response of the system.

6.6.2 Finite element model

In Fig. 6.3(c) we plot the results of finite element numerical modelling of hole arrays on a lossless silicon substrate (blue dashed line). We model the hole array using the Ansoft HFSS v.11 finite element modelling package, approximating the gold layer as perfect electrical conductor, modeling the silicon substrate as a dielectric with complex permittivity of $\varepsilon_s = 11.85 + 0.56i$. We model the photo-excited silicon as a 125nm-thick region in the substrate immediately below the hole, with a dielectric function determined through phase-resolved direct transmission measurements of the photo-excited silicon. We define the modulation $P$ in the same way as for the experimental measurements, $P = (I_0 - I_{pm})/I_0$ at resonance. We approximate the structure as being of semi-infinite extent in the plane containing the holes; master-slave boundaries are used on the side of a unit cell containing a single hole. Above and below the holes we impose radiation boundaries (in the air superstrate and silicon substrate). This simple model without loss predicts that $P$ increases monotonically upon decreasing the hole size. The non-monotonic trend of photomodulation with hole size seen in our experiment is due to intrinsic losses within our silicon substrate; a low concentration of impurity charge carriers in the crystalline silicon contribute an imaginary component to the permittivity of the substrate, which reduces the surface mode lifetime. In the 25 and 35 $\mu$m holes the surface mode lifetime is not limited by phase-retardation across the holes, but instead by absorption in
the silicon substrate - this in turn limits the interaction of the surface modes with the photo-excited silicon. By introducing an imaginary component to the dielectric constant of the silicon substrate in our Finite Element model of $0.56i$ at 0.85 THz (determined by phase-resolved THz transmission measurements through the silicon substrate) we can accurately reproduce the experimental results as the red line in Fig. 6.3(c). The model incorporating loss exhibits the non-monotonic trend in photomodulation with hole size seen in the experiment, and further demonstrates the role of surface mode lifetime in determining the modulation. The modelled modulation for the given fluence is actually slightly higher than that measured in experiment; this is because we do not fully recover the narrow mode width for transmission through the smallest holes - the instrumental frequency resolution of the terahertz spectrometer is limited by reflections within the silicon substrate.

## 6.7 Modulation efficiency

Our results suggest that if one could limit the intrinsic losses in an array of very small holes fabricated on a semiconductor, the photomodulation effect could become extremely efficient. Our modelling in Fig. 6.3(c) indicates that for an array of 25 µm holes on a lossless silicon substrate a fluence of less than 0.2 J/m² will produce a photomodulation ratio of near unity. This photomodulation ratio corresponds to the intensity ($I_0/I_{pm}$) changing by a factor of 600, compared to a factor of only 1.5 for the unstructured plain silicon surface. If we compare this to other reports of photo-modulation of terahertz in literature using silicon with similar densities of photoexcited charge carriers, a silicon-based photonic crystal structure has been shown to modulate terahertz intensity by a factor of approximately 12,
and a silicon-based waveguide structure\textsuperscript{150} gives an intensity change of 1.4 under a continuous-wave excitation. In our lossy experimental system, the maximum intensity change attained (with the 55 µm hole array) is a factor of 2.6, very comparable with other measured photomodulation measurements in hole array structures\textsuperscript{134,139}. In order to approach the modelled factor of 600 one would need to reduce the levels of scattering and loss in the system - this can be achieved by using ultra high-purity semiconductor substrates and cooling to cryogenic temperatures\textsuperscript{146}. Additionally, the photoexcited carrier lifetime in silicon is relatively long: for modulation by a pseudo continuous wave light source this long carrier lifetime is useful, as one can build up a high carrier density with a relatively weak light source. However, in pulsed applications the long lifetime imposes a maximum repetition rate of switching. This constraint could be avoided by using direct band gap semiconductors such as GaAs instead of silicon\textsuperscript{141}.

\textbf{6.8 Conclusions}

In conclusion, we have shown how photomodulation of the EOT in our hole array structures is governed by the effects of surface mode propagation. By adding a metal hole array structure to the surface of a silicon substrate we are able to enhance the response of the silicon to photoexcitation. In particular we find that when surface mode lifetime is limited (such as by intrinsic loss in the substrate) the photomodulation enhancement is similarly limited. However our modelling shows that by following the strategies for loss-reduction and increasing the surface mode lifetime extremely high efficiencies for optical modulation could be achieved using this scheme. Such efficient optical modulators could find applications as non-linear...
switches in optical circuitry and related systems.
Chapter 7

Conclusions and evaluations

7.1 Semiconductor surface plasmons in slits

In Chapter 3 (experiments on a subwavelength semiconductor slit cavity) we can draw conclusions as to how the characteristics of the propagating surface plasmons in the slit affect the nature of the resonant transmission - specifically showing how the effective index of the mode and propagation length of the coupled surface plasmons change the resonant transmission frequency and resonance width. We conclude that the shift in resonance position when the dimensions of such a slit are changed is an interplay between an increase in effective mode index for the propagating surface plasmon, the effects of changing the boundary conditions at the end of the slits.

7.2 Terahertz surface plasmon spectroscopy

We are able to conclude from the experiments of Chapter 4 that the confined electric field of a terahertz surface plasmon on Indium Antimonide is sensitive to the presence
of subwavelength films on the surface, and that at 1 THz this can be demonstrated for low-index dielectric films as thin as 500nm. From analytical modeling we can see that a realistic biological analyte (with lossy dielectric function) will be even more readily detectable. From an experimental standpoint we are able to conclude that, using the blade-edge coupling geometry, it is not possible to properly interrogate the surface eigenmode on a gold-air interface at terahertz frequencies; we conclude that this is due to the evanescent decay length of the mode away from the surface being longer than the length over which the mode is propagated.

7.3 Hole-array transmission

From the experiments in Chapter 5 we are able to draw relatively broad conclusions about the role of surface modes in mediating transmission in hole array structures. Not only are we able to demonstrate that the transmission is mediated by surface modes, but we are able to link the lifetime of the mode to the characteristics of the resonances. We are able to assess the relative importance of the two transmission channels in determining the transmission of the hole arrays, and finally to show that if one were to build a hole-array in which the surface-mode transmission channel predominates in the electromagnetic response of the structure then the resonances would have an exceptionally high Q-factor.

7.4 Photomodulation in hole-arrays

The primary conclusion from Chapter 6 is that a hole array structure can greatly enhance the response of a silicon surface to photoexcitation, and that this enhance-
ment is linked to the coupling of surface modes to the hole array / silicon interface. We show that if the surface mode lifetime can be increased (through alteration of the structure and minimisation of losses) then the photomodulation efficiency of the structure can be improved still further; this is linked to the previous conclusion regarding the Q-factor of the resonance in the array.

7.5 Experimental methods

In the above experiments we have shown many of the benefits of terahertz time-domain spectroscopy for experiments in plasmonics. In particular the availability of phase information is crucial for the experiments measuring mode index (Chapter 3) and wavenumber-shift (Chapter 4). The time-domain information alone is valuable for determining the resonance lifetimes in Chapter 5.

We have also encountered some limitations to the technique. Frequency resolution can be a constraint, as in Chapter 5, in determining the width of the narrowest resonances. In a related effect, the Fourier transform of noise spectra over a finite time-domain window can introduce spurious features to the frequency domain.

The experiments of Chapter 6 have shown that the coupling of terahertz time-domain spectroscopy with photoexcitation by optical pulses can be a very powerful technique; as well as being a convenient way to demonstrate all-optical switching and modulation, the pump-probe measurements actually provide evidence of the interplay between mode lifetime and structure transmission.
7.6 Modelling techniques

Finite element modelling with HFSS (used in several parts of this thesis) has provided a great deal of flexibility and versatility for confirming the results of experiments, and has played a part in planning and designing certain structures. In particular, the simulation of the SP propagation experiment in Chapter 4 demonstrates the usefulness of FEM in producing accurate results for systems which would otherwise be very complex to model; similarly the photoexcited hole-array structure of Chapter 6 is difficult to represent in an analytical formulation.

Time-domain terahertz measurements give sufficient information that we can compare them, in some cases, to very straightforward analytical models; in particular when we are able to measure mode index and wavenumber shift we can compare these directly to the well-known results for planar surface plasmons, such as in Chapters 3 and 4.

The modal matching technique used in Chapter 5 to simulate the transmission of hole arrays has the advantage of being much less computationally intensive than finite element modelling (solution times being in minutes rather than hours or days); this allows for highly accurate solutions (not limited by FEM mesh resolution). Additionally it can be important to consider the components of transmission in isolation through inspection of the underlying expressions, which cannot be achieved in a Finite Element model.
7.7 Future work

From all of the above work we can see that surface plasmon structures for terahertz frequencies are realisable and can show interesting aspects of physics. They are tunable both through the alteration of structural dimensions and by changing the material properties, especially in semiconductors in which material response can be altered rapidly and dynamically. There is a great deal of work which can still be carried out using these techniques - for instance, many of the other optical plasmonic systems such as particle plasmons, grating-coupled plasmons and plasmonic waveguides should all scale to the terahertz frequencies. There are many metal-based structures from the microwave range which support surface modes that could be scaled to give plasmon-like behaviour in the terahertz range, as well as a wealth of structures which could be considered for experiments in to EOT and surface-mode mediated transmission.

Finally, there is potential for future work applying terahertz surface modes directly to the measurement of biological or chemical experiments, or applying the hole-array structures for use as narrowband filters or efficient photo-switches.
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Appendix A

Modal matching model

This appendix covers the formalism of the modal matching model (developed by Dr. Euan Hendry) used for calculations in Chapter 5.

We begin by defining expressions for the electric and magnetic fields in the three regions of a hole array, indicated as numbers on Fig. 5.1: in the incident vacuum region (1), inside the holes (2), and in the substrate (3). For simplicity, note that in all the following equations we omit the time $t$ dependent component to the fields, $e^{i\omega t}$, where $\omega$ is the radial frequency. We express the electric field in the vacuum region ($E^1_x$) as a sum of normally incident, unit plane waves polarized in the $x$-direction and a two-dimensional Fourier-Floquet expansion of diffracted orders. Inside the holes, approximating the metal as being perfectly conducting (a reasonable approximation at THz and microwave frequencies\textsuperscript{151}), the electric field ($E^2_x$) is expressed by the fundamental mode in a square cavity of width $a$, while in the substrate we have another Fourier-Floquet expansion of diffracted orders ($E^3_x$).
These definitions amount to:

\[ E_x^1 = \exp(ik_0 z) + \sum_{m_1, m_2} r^{m_1, m_2} \Psi^{m_1, m_2} \exp(-i k_z^{m_1, m_2} z), \quad (A.1a) \]

\[ E_x^2 = B \sin(\frac{\pi y}{a}) \exp(i q_z z) - C \sin(\frac{\pi y}{a}) \exp(i q_z z), \quad (A.1b) \]

\[ E_x^3 = \sum_{n_1, n_2} t^{n_1, n_2} \Psi^{n_1, n_2} \exp(i k_z^{n_1, n_2} z), \quad (A.1c) \]

where \( \Psi^{m_1, m_2} = \exp(i \frac{2m_1 \pi}{d} x) \exp(i \frac{2m_2 \pi}{d} y) \). The integer pairs \( m_1, m_2 \) and \( n_1, n_2 \) denote the diffracted orders from the grating of pitch \( d \) on the incident \( m \) and the substrate \( n \) sides of the hole array. The factors \( r^{m_1, m_2} \) and \( t^{n_1, n_2} \) describe the complex electric field reflection and transmission coefficients respectively. The factor \( B \) describes the electric field amplitude of the decaying wave in the cavity, and the factor \( C \) describes the field amplitude of the wave reflected from bottom of the cavity.

The wavevector associated with a particular diffracted order is denoted by \( \mathbf{k} \). The \( z \) component of the wave-vector in the incident and substrate regions can be written as

\[ k_z^{m_1, m_2} = \sqrt{k_0^2 - \left(\frac{2m_1 \pi}{d}\right)^2 - \left(\frac{2m_2 \pi}{d}\right)^2}, \quad (A.2a) \]

\[ k_z^{n_1, n_2} = \sqrt{\varepsilon_s k_0^2 - \left(\frac{2n_1 \pi}{d}\right)^2 - \left(\frac{2n_2 \pi}{d}\right)^2}, \quad (A.2b) \]

where \( c \) is the speed of light, and \( k_0 = \omega/c \). Note that we consider only the case where the superstrate is vacuum, i.e with a refractive index of unity. The propagation constant in the cavity is

\[ q_z = \sqrt{k_0^2 - (\pi/a)^2}. \quad (A.3) \]
In agreement with previous observations\textsuperscript{68}, we find only minor perturbation to the results for thin samples when we include higher order waveguide modes.

We can obtain the $z$ components of the electric field in the three regions of space, and subsequently expressions for the magnetic field $H$, through the free space Maxwell relations $\nabla \cdot E = 0$ and $\nabla \times E = -\mu_0 \partial H / \partial t$. These give the $x$ and $y$ components of the electric and magnetic fields in all regions in terms of the set of unknowns $r$, $t$, $B$ and $C$. We can eliminate some of these unknowns through imposition of boundary conditions stating that both the $x$ and $y$ components of the electric field must be continuous at the vacuum-substrate interfaces over the entire unit cell, i.e. continuity $z = 0$ and $z = h$ where $h$ is the depth of the holes in the array. In contrast the magnetic field components are continuous only at the hole aperture.

Matching the electric field in regions 1 and 2 at $z = 0$, and in regions 2 and 3 at $z = h$ (i.e. multiplying by $\Psi^*$ and integrating over $x$ and $y$ from 0 to $d$), and taking into account the orthogonality of the eigenmodes of the system, yields

\begin{equation}
\delta^{m_1,m_2} r^{m_1,m_2} d^2 + r^{m_1,m_2} d^2 = (B - C) S^{m_1,m_2}_1 \tag{A.4a}
\end{equation}

\begin{equation}
 t^{m_1,m_2} e^{ik_{n_1,n_2} h} d^2 = (B e^{iq_z h} - C e^{-iq_z h}) S^{m_1,m_2}_1 \tag{A.4b}
\end{equation}

\begin{equation}
 S^{m_1,m_2}_1 = \int_0^a \int_0^a \sin \left( \frac{\pi y}{a} \right) \times exp \left( -i \frac{2m_1 \pi}{d} y \right) \times exp \left( -i \frac{2m_2 \pi}{d} y \right) dxdy, \tag{A.4c}
\end{equation}

where $\delta^{m_1,m_2}$ represents the Kronecker delta function, $\delta(m_1) \delta(m_2)$.

By considering continuity of the $H$ field over the holes at $z = 0$ and $z = h$ respectively we can obtain the pair of equations A.5a and A.5b - We are essentially
multiplying $H$ fields by $\sin(\frac{\pi y}{a})$ and integrating from 0 to $a$ for $x$ and $y$:

$$k_0 \frac{2a^2}{\pi} - \sum_{m_1,m_2} r^{m_1,m_2}(k_z^{m_1,m_2} + \frac{1}{k_z^{m_1,m_2}}(\frac{2m_1\pi}{d})^2)S_2^{m_1,m_2}$$

$$= (B + C)q_z \frac{a^2}{2} \quad (A.5a)$$

$$\sum_{n_1,n_2} t^{n_1,n_2}(k_z^{n_1,n_2} + \frac{1}{k_z^{n_1,n_2}}(\frac{2n_1\pi}{d})^2)e^{ik_z^{n_1,n_2}h}S_2^{n_1,n_2}$$

$$= (B e^{iq_zh} + C e^{-iq_zh})q_z \frac{a^2}{2} \quad (A.5b)$$

$$S_2^{m_1,m_2} = \int_0^a \int_0^a \sin(\frac{\pi y}{a}) \exp(i \frac{2m_1\pi}{d} x) \exp(i \frac{2n_2\pi}{d} y) dx dy \quad (A.5c)$$

It is then straightforward to solve equations A.4a, A.4b, A.5a and A.5b eliminating the coefficients $B$ and $C$ to obtain the complex reflection and transmission coefficients, $r(m_1, m_2)$ and $t(n_1, n_2)$:

$$r^{m_1,m_2}(\omega) = \frac{4a^2 k_0 S_1^{m_1,m_2}}{\pi} - \delta^{m_1,m_2} \quad (A.6a)$$

$$t^{n_1,n_2}(\omega) = \frac{4a^2 k_0 S_1^{n_1,n_2}}{\pi} \quad (A.6b)$$

$$Q = \sum_{m_1,m_2} S_1^{m_1,m_2} S_2^{m_1,m_2}(k_z^{m_1,m_2} + \frac{1}{k_z^{m_1,m_2}}(\frac{2m_1\pi}{d})^2)$$

$$+ \sum_{n_1,n_2} S_1^{n_1,n_2} S_2^{n_1,n_2}(k_z^{n_1,n_2} + \frac{1}{k_z^{n_1,n_2}}(\frac{2n_1\pi}{d})^2) \quad (A.6c)$$

Solving the three equations in A.6 constitutes a complete simulation of the complex reflection and transmission coefficients of the hole array. Typically, we find that convergence was obtained by summing over the first three diffracted orders.

We are interested in the frequency dependent zero order reflected and transmitted
power, $R$ and $T$, given by:

\begin{align}
R^{0,0}(\omega) &= |r^{0,0}|^2 \\
T^{0,0}(\omega) &= |t^{0,0}\sqrt{\varepsilon_s}|^2
\end{align}

(A.7a)  
(A.7b)

This concludes the formalism of our model. Note that, in order to compare our model with experimental data, we normalize $T^{0,0}(\omega)$ by the transmittance of an air-silicon interface, which take as being 0.70 throughout the THz frequency range.