GRATING-COUPLED SURFACE PLASMONS FOR ENHANCED TERAHERTZ EMISSION

Proefschrift

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus prof. ir. K. C. A. M. Luyben,
voorzitter van het College voor Promoties,
in het openbaar te verdedigen op dinsdag 1 april 2014 om 12.30 uur

door

Gopika Ramanandan KOTTAYI PILAPPARA

Master of Science in Photonics
Cochin University of Science and Technology, Cochin, India
geboren te Kozhikode, India
This work was funded by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) and the Stichting voor Technische Wetenschappen (STW)

Copyright © 2014 by G. R. Kottayi Pilappara

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means: electronic, mechanical, photocopying, recording or otherwise, without prior written permission of the author.


Printed in the Netherlands by Ipskamp Drukkers, Enschede.

A free electronic version of this thesis can be downloaded from: 
http://repository.tudelft.nl

Author email: g.r.kottayipilappara@tudelft.nl
To my parents.
Cover photo credit:
Parvathi Ramanandan
Summary
Grating-coupled surface plasmons for enhanced terahertz emission

The colors we see around us correspond to light of various wavelengths. Our eye is sensitive only to a small range of wavelengths which ‘light’ consists of. Other kinds of ‘invisi
in this thesis are outlined below.

To form the cuprous oxide thin film, we have heated Cu thin films at elevated temperatures in the ambient atmosphere of the lab. This is an important step, since we wanted the copper film to completely oxidize into cuprous oxide, but wanted to avoid the formation of cupric oxide. This made us think about a method to characterize the oxidation of copper thin films. In fact we have shown that terahertz radiation itself could be used to study the oxidation kinetics of thin films of copper, deposited on silicon substrates. By using a terahertz time-domain spectroscopy setup, we studied in-situ the oxidation of Cu thin films. While trying to calibrate the transmission of terahertz radiation through thin copper films deposited by evaporation techniques, we also found that percolation causes the terahertz-optical properties of these thin films to differ from that of bulk metal. In fact, thin films of metals like copper start to act as a metal only after depositing a minimum thickness, which is known as the percolation threshold thickness.

A logical explanation for the terahertz emission from gold-cuprous oxide junctions requires them to behave as a diode. However, scientific literature seems to suggest that junctions formed by depositing gold on cuprous oxide do not show characteristics of a diode. Through a part of the research carried out in this thesis, we show that heating copper on gold to form junctions with cuprous oxide, results in the inter-diffusion of gold and copper resulting in the formation of an alloy of these metals at the interface. Our measurements suggest that this alloy forms a junction with cuprous oxide, which has diode-like behavior. We have studied the optical properties of this alloy, through techniques like ellipsometry, x-ray diffraction etc.

A considerable portion of this research is dedicated to the enhancement of terahertz radiation emitted from metal/semiconductor junctions using surface plasmons. Vaguely resembling waves on the surface of water, surface plasmons are waves of electrons at the interface between a metal and a dielectric. Surface plasmons have a very interesting property that their energy is confined/localized to the interface. Excitation of surface plasmons increases the amount of pump laser light absorbed by the gold-cuprous oxide thin films, resulting in enhanced terahertz emission. To excite surface plasmons, we fabricated gold nano-gratings and then deposited cuprous oxide over it. We have shown that the important factor for enhanced terahertz emission is to increase the absorption at a region where it matters the most for terahertz generation, which is the semiconductor region close to the metal/semiconductor interface.
Plasmon excitation can also result in terahertz emission from gold gratings without any extra-material deposited over it. We show that we can generate terahertz radiation from gold gratings, after the excitation of surface plasmons. The mechanism by which terahertz radiation is generated from gold thin films has been a matter of debate, with several explanations found in the literature. An important indicator of the terahertz emission mechanism is the dependence of the emitted terahertz radiation on the incident pump power. The emitted terahertz power shows a second-order dependence on the incident pump laser power, which is in contradiction with the higher order pump-power dependence observed by other groups using similar gratings. We have explored the different possible mechanisms by also measuring the azimuthal-angle dependence and by measuring the polarization of the terahertz radiation emitted from these gratings. An interesting aspect of our study is that it hints at the possibility of a new generation mechanism, transient photon-drag currents, and could lead us to interesting revelations on the terahertz generation from metal surfaces in general.

In summary, we have studied the characteristics of metal/semiconductor thin film terahertz emitters formed using gold and cuprous oxide. We have explored the use of gratings for coupling surface plasmons and thus enhancing the strength of terahertz emitters made of metal/semiconductor thin films. This concept has also been extended to enhancing the terahertz emission from pure gold thin films to study a possibly new THz generation mechanism.

Gopika Ramanandan Kottayi Pilappara, March 2014
Samenvatting
Traliegekoppelde oppervlakteplasmonen voor versterkte terahertz emissie

De kleuren die we om ons heen zien corresponderen met licht van verschillende golflengtes. Ons oog is alleen gevoelig voor een smalle golflengteband waar licht uit bestaat. Andere vormen van onzichtbaar licht zijn ook bekend: röntgenstraling, gebruikt om botten af te beelden, microgolven om ons eten op te warmen in de keuken, en ook radio golven die gebruikt worden voor informatie overdracht. Terahertzstraling is een vergelijkbare vorm van licht die onzichtbaar is voor onze ogen. De golflengtes liggen tussen dat van infrarood en microgolfstraling in. Terahertzstraling kan zich voortplanten door veel materialen, zoals hout, papier, kleren, plastic etc. Veel chemicaliën en biomoleculen hebben absorptielijnen op terahertz frequenties, wat terahertz licht geschikt maakt voor spectroscopie. Deze interessante eigenschappen hebben mensen laten denken aan verschillende toepassingen, zoals veiligheidscameras, identificatie van medicijnen, etc., voor het gebruik van terahertz straling.

Echter, er zijn verschillende aspecten van terahertztechnologie die verbeterd kunnen worden voor genoemde toepassingen. Eén van deze is de bron van terahertzstraling. Wanneer er gedacht wordt aan een geschikte bron van terahertzstraling wordt naar verschillende aspecten gekeken, zoals de intensiteit, het spectrum en de kosten. Gezien de groei van on-chip optische sensoren is het waarschijnlijk dat toekomstige terahertztechnologie gebruik gaat maken van geminiatuuriseerde terahertz bronnen. Een soort terahertz bron die onderzocht is in dit proefschrift is een junctie gevormd tussen een dunne goudlaag en een dunne koper(I)oxide laag. Koper(I)oxide is een oxide van het meest voorkomende metaal in de natuur, namelijk koper. Wanneer een femtoseconde puls van infrarood licht zon junctie van koperoxide en goud belicht, wordt er een puls van terahertz straling uitgezonden. De straling van deze emitters is breedbandig en is sterk genoeg om te gebruiken voor spectroscopie. In dit proefschrift zijn de eigenschappen van deze emitters bestudeerd en er is een techniek onderzocht om de sterkte van terahertz emissie te vergroten door het gebruik van nanostructuren,
die de excitatie van oppervlakteplasmonen mogelijk maakt. De hoofdlijnen van het onderzoek, zoals beschreven in het proefschrift, worden hieronder geschetst.

Om de dunne laag koperoxide te vormen wordt een dunne laag koper verhit in de lucht. Dit is een belangrijke stap omdat we de koperlaag helemaal willen omzetten in koper(I)oxide, terwijl de vorming van koper(I)oxide moet worden voorkomen. Dit heeft ons laten nadenken over een methode om de oxidatie van de koperoxide laag te karakteriseren. We laten zien dat terahertz straling zelf gebruikt kan worden om de oxidatiekinetica van dunne lagen koper, gedeponeerd op silicium substraten, te bestuderen. Door het gebruik van een terahertz tijd-domein spectroscopie opstelling, hebben we in-situ de oxidatiekinetica van dunne koperlagen bestudeerd. Toen we probeerden om de transmissie van terahertz straling door dunne lagen koper, gedeponeerd door het gebruik van verschillende opdamptechnieken, te kalibreren, hebben we ook gevonden dat percolatie er voor zorgt dat de terahertz-optische eigenschappen van deze dunne oppervlakken verschilt van dat van bulkmetaal. Dunne oppervlakken van metalen zoals koper gedragen zich alleen als metaal indien er een bepaalde minimumdikte gedeponeerd wordt, bekend onder de term percolatiedrempeldikte.

Een logische verklaring voor de terahertz emissie van goud-koper(I)oxide juncties is dat deze zich als diodes gedragen. Echter, wetenschappelijke literatuur lijkt te suggereren dat juncties die gevormd worden door depositie van goud op koper(I)oxide niet te karakteriseren zijn als een diode. In een gedeelte van het onderzoek uitgevoerd in dit proefschrift laten we zien dat het verwarmen van koper op goud om juncties met koper(I)oxide te vormen, resulteert in de inter-diffusie van goud en koper resulterend in de vorming van een legering van deze metalen bij het raakvlak. Onze metingen suggereren dat deze legering een junctie vormt met koper(I)oxide, die zich als een diode-achtige overgang gedraagt. We hebben de optische eigenschappen van deze legering bestudeerd met technieken als ellipsometrie, röntgendiffractie etc.

Een aanzienlijk gedeelte van dit onderzoek is gewijd aan de versterking van terahertz straling, geëmitteerd van metaal-halfgeleider juncties, door het gebruik van oppervlakteplasmonen. Oppervlakteplasmonen zijn golven van elektronen op het grensvlak van een metaal en een diëlektrisch materiaal. Deze golven hebben heel vaag wel iets weg van watergolven. Oppervlakteplasmonen hebben de interessante eigenschap dat hun energie beperkt/gelokaliseerd is tot dichtbij het raakvlak. Excitatie van oppervlakteplasmonen verhoogt de hoeveelheid geabsorbeerd pomp licht bij de goud-
koper(I)oxide dunne lagen, resulterend in verhoogde terahertz emissie. Om oppervlakteplasmonen te exciteren hebben we gouden nanotralies gefabriceerd en daar koper(I)oxide op gedeponeerd. We hebben aangetoond dat de belangrijkste factor voor de versterkte emissie de verhoogde absorptie vlak bij het metaal/halfgeleider raakvlak is, het gebeid dat het belangrijkste is voor de terahertz generatie.

Plasmon excitatie kan ook resulteren in terahertz emissie van goudtralies zonder dat daar een ander materiaal op is gedeponeerd. We laten zien dat we terahertz straling kunnen genereren van goudtralies, na excitatie van oppervlakteplasmonen. Het mechanisme waardoor terahertz straling wordt gegenereerd bij dunne goudoppervlaktes staat ter discussie, en er kunnen verschillende verklaringen in de literatuur worden gevonden. Een belangrijke indicatie van het terahertzemissiemechanisme is de afhankelijkheid van terahertz emissie van het invallende laser pompvermogen. De geëmitteerde terahertz straling heeft een kwadratische afhankelijkheid van het invallende laser pompvermogen, wat tegenstrijdig is met de hogere-orde afhankelijkheid gemeten door andere groepen met vergelijkbare tralies. We hebben verschillende mechanismes onderzocht door ook de azimuthale hoekafhankelijkheid te meten en ook door de polarisatie van het geëmitteerde terahertz licht te meten. Een interessant aspect van onze studie is dat we hints hebben gevonden van de mogelijkheid van een nieuw excitatie mechanisme, photon-drag stromen, wat zou kunnen leiden naar interessante verklaringen voor terahertz generatie van metalen.

Samenvattend, hebben we de karakteristieken bestudeerd van metaal/halfgeleider dunne laag terahertz emitters gevormd door het gebruik van goud en koper(I)oxide. We hebben het gebruik van tralies om oppervlakteplasmonen te genereren om aldus terahertz emitters, gemaakt van dunne lagen metaal/halfgeleider, te versterken onderzocht. Dit concept is ook uitgebreid naar de versterkte terahertz emissie van pure dunne lagen goud om een mogelijk nieuw terahertzgeneratiemechanisme te onderzoeken.

Gopika Ramanandan Kottayi Pilappara, March 2014
## Contents

**Summary** v  
**Samenvatting** ix  
**Contents** xiii  

### 1 Introduction
1.1 Introduction to THz radiation .......................... 1  
1.2 Applications of THz radiation .......................... 3  
1.3 THz generation using femtosecond laser pulses ......... 4  
  1.3.1 Photo-conducting antenna ........................... 4  
  1.3.2 Optical rectification ................................. 5  
  1.3.3 Current surge on semiconductor surfaces .......... 6  
1.4 Plasmonics ............................................. 7  
1.5 This thesis ........................................... 9  

### 2 Plasmon facilitated THz emission from gold gratings 11  
2.1 Introduction to plasmonics ............................... 11  
  2.1.1 Dispersion relation of surface plasmons .......... 12  
  2.1.2 Properties of surface plasmons .................... 13  
2.2 Grating coupling of surface plasmons ................... 15  
  2.2.1 Plasmon excitation with a metal grating for non-zero azimuthal angles .............................. 18  
2.3 THz emission from gold thin films - a literature survey 19  
  2.3.1 Optical rectification ................................. 19  
  2.3.2 Multiphoton excitation .............................. 20  
  2.3.3 Other mechanisms ............................... 22  
2.4 THz emission from gold gratings ....................... 23  
  2.4.1 Azimuthal-angle dependence .......................... 26  
2.5 Etch depth dependence ................................ 27  
2.6 Discussion ........................................... 29
3 Oxidation kinetics of Cu thin films
   3.1 Introduction .............................................. 33
   3.2 THz transmission through oxidizing Cu thin films .......... 34
      3.2.1 Experiment ......................................... 35
      3.2.2 Results ........................................... 36
   3.3 Thickness-dependent THz transmission ....................... 39
      3.3.1 Percolation ......................................... 41
      3.3.2 Calibration of THz transmission ..................... 42
   3.4 Oxidation kinetics and Arrhenius equation .................. 43

4 THz emission from Cuprous oxide thin films
   4.1 Introduction .............................................. 47
   4.2 Metal-Semiconductor (Schottky) junctions ................. 48
   4.3 Cuprous oxide as a semiconductor ........................ 51
   4.4 THz generation from Au/Cu$_2$O thin films ................ 53
      4.4.1 Sample preparation .................................. 53
      4.4.2 Experimental set-up and results ..................... 53
   4.5 Interface between gold and thermally formed Cu$_2$O ...... 56
   4.6 Variable-Angle Spectroscopic Ellipsometry ............... 59
   4.7 Thickness dependence of pump power absorption and THz emission ........................................ 62
   4.8 Multilayer reflection: Calculation and experiment .......... 64
   4.9 Application: Tapered waveguide .......................... 66

5 Plasmon-enhanced THz emission from Schottky junctions
   5.1 Introduction .............................................. 71
   5.2 The concept of a plasmon-enhanced Schottky emitter ....... 72
      5.2.1 Plasmon excitation at the Au/Cu$_2$O interface ....... 73
   5.3 Sample fabrication and characterization ..................... 75
   5.4 Experimental Setup ....................................... 78
   5.5 Plasmon-enhanced THz emission ............................ 79
   5.6 Reflection spectroscopy measurements ....................... 83
      5.6.1 p-polarized incident light .......................... 86
      5.6.2 s-polarized incident light .......................... 90
   5.7 THz emission as a function of the grating periodicity ....... 94
   5.8 Azimuthal angle dependence ................................ 99
      5.8.1 Enhanced THz emission: significance of exciting plasmon modes ........................................ 99
      5.8.2 Reflection spectra vs azimuthal angle ............... 101
      5.8.3 Near-field analysis .................................. 104
   5.9 Conclusion .................................................. 106
6 Conclusions and Outlook
Chapter 1

Introduction

1.1 Introduction to THz radiation

Terahertz radiation (THz) is the name used for electromagnetic radiation in a region of the electromagnetic spectrum which is positioned in-between the microwave and the infrared domains. The THz range includes frequencies from 0.1-10 THz. To get an idea of the wavelengths involved, 1 THz corresponds to a wavelength of 300 µm, a wavenumber of 33 cm$^{-1}$, and a photon energy of 4.14 meV.

Historically the THz frequency range has been known as the THz gap, due to the lack of availability of suitable sources, detectors and other technologies compared to that in the electronic and photonic domains. This location of THz radiation in the electromagnetic spectrum has also given it a multidisciplinary character, and attempts to fill the THz gap have come from both the optical and the electronic domains.

A good overview of the development of various THz sources can be found in the articles [1, 2, 3]. The developments from the electronic side include electron-beam backward wave oscillators and recombination diode lasers, operating at sub-mm wavelengths [4]. High frequency Gunn and IMPATT diodes have been demonstrated to work quite well for frequencies in the sub-THz range [5].

From the optics side, gas lasers were developed in the 1960s due to a desire to have coherent sources of far infrared radiation. Stimulated emission of far infrared wavelengths between 23 µm and 79 µm was demonstrated by Crocker et al. [6] in 1964 using pulsed electrical discharges in water vapor. An important recent development regarding continuous wave THz sources, is the invention of the quantum cascade laser (QCL) by Faist et al. [7] in 1994. The first QCL in the THz range was fabricated by Köhler et al. [8]
in 2002, and operated at a frequency of 4.4 THz.

Today, an important branch of THz technology is time-domain spectroscopy. The basic idea of THz time-domain spectroscopy is as follows: Short pulses of THz radiation are passed through a sample to probe its material properties. The THz pulses get modified after passing through the sample and are detected using a coherent detection technique, which measures the time-dependent electric field of the THz pulses. Thus, both amplitude and phase information of the THz pulses are obtained, which is the main advantage of THz-TDS. By Fourier-transforming the measured time-dependent electric field of the THz pulse, we can immediately obtain the frequency-spectrum.

The generation and detection of coherent THz pulses is therefore an important part of THz time-domain spectroscopy. It was shown by Auston et al. [9] in 1984 that the illumination of certain electrically biased semiconductors with femtosecond pulses gives rise to the generation of sub-picosecond electrical pulses, which can be coupled into free space using antennas. Such photoconductive antennas can be said to be one of the most used sources of pulsed, coherent THz radiation. A comprehensive review on the development of photoconductive sources is given in [10] and [11]. Later in this chapter, we will also look at other methods of generating THz pulses using ultrafast lasers.

Detection of coherent THz radiation involves a gated detection technique, where the THz detector is gated using a probe pulse. The detector output is proportional to the amplitude and sign of the THz electric field at a particular moment of time. By changing the delay between the probe pulse and the THz pulse, it is possible to trace the time profile of the THz pulse in a stroboscopic manner. The common detection techniques employ either a photoconductive antenna or electro-optic detection [12] to facilitate the time gating. In the work described in the following chapters, we have used the electro-optic detection technique, where the electric field of the THz pulses modifies the birefringence of a suitable detection crystal. This is
measured as a change in the polarization state of the probe pulse. A THz time-domain spectroscopy system used for the study of oxidation of Cu thin films, is described in section 3.2.1.

1.2 Applications of THz radiation

Perhaps the most important feature of THz radiation is that it can be partially transmitted by a number of materials, such as paper, cloth, leather, polymers, etc, which are opaque to visible light. This unique property of THz radiation, to look through materials, makes it suitable for applications in security and screening \[13, 14\], quality analysis \[15\] etc.

Another important aspect is that various crystalline vibrations and molecular rotational transitions of various materials and gases also lie in this frequency range. THz spectroscopy has become an important tool to understand the interaction of biomolecular systems with water\[16\]. Another application of THz technology is the identification of materials using their spectral signature in this frequency range. Kawase et al. \[17\] demonstrated a technique to identify drugs concealed in envelopes using terahertz imaging. THz spectroscopy can also differentiate between the polymorphs of the same material. For example, Chakkittakandy et al. \[18\] demonstrated that THz spectroscopy can identify the different polymorphs of mannitol, a product used in the pharmaceutical industry. More pharmaceutical applications of THz spectroscopy can be found in Refs. \[15, 19\].

Applications of THz imaging in the biomedical sciences, although still the subject of discussion, should be mentioned as well. A good review of this topic is provided by Pickwell and Wallace \[20\], discussing applications which range from spectroscopy of crystalline drugs to imaging of skin cancer.

THz imaging has become a valuable tool for art historians, due to its capability to see through the various layers in a painting \[21\], and to determine the properties of the paint used by the artist \[22\].

A major hurdle for imaging with THz radiation is it’s large wavelength, which limits the resolution which can be achieved. This is a direct consequence of the laws of diffraction, which imply that with a conventional microscope, it’s not possible to see “sharper” than about half of a wavelength. For THz light with a wavelength of 300 \(\mu\)m, this means that the sharpest features that can be observed would be about 150 \(\mu\)m. The concept of near-field scanning optical microscopy using apertures was used to overcome the diffraction limit and to image with sub-wavelength spatial res-
olution [23, 24]. In 2002, van der Valk and Planken [25] demonstrated an apertureless method to obtain sub-wavelength resolution in THz imaging by using a sharp copper tip and selective detection of THz light near the tip through electro-optic detection. A number of applications for THz near field imaging has come up, primarily in understanding and exploring the laws of physics, which would be more difficult to do with visible light [26, 27]. High resolution THz near-field imaging has been used as an effective tool to map mobile carriers in semiconductor nanodevices [28].

1.3 THz generation using femtosecond laser pulses

1.3.1 Photo-conducting antenna

In a photoconducting antenna, THz pulses are created by the acceleration of photo-excited charge carriers in a semiconductor in an electric field applied by biasing two electrodes on the surface of the semiconductor. A pair of metal electrodes is deposited on a semiconductor, as shown in Fig. 1.2. A DC bias is applied between the electrodes. Laser pulses, with photons having an energy greater than the band-gap energy of the semiconducting material, are focussed onto the area in between the electrodes, generating electron-hole pairs. These free charge carriers are accelerated by the DC electric field and simultaneously decay due to recombination. The impulse current generated due to this acceleration of the charge carriers, radiates pulses of THz electromagnetic waves [11].

The radiated electric field $E_{THz}$ is proportional to the rate of change of the induced current $J(t)$ [29]:

$$E_{THz} \propto \frac{\partial J(t)}{\partial t}. \quad (1.1)$$

The photo current density $j(t)$ can be described as a convolution of the optical intensity profile of the pulse incident on the sample $I(t)$, and the impulse response of the photoconductive antenna, $n(t)qv(t)$, where $n(t)$ is the density, $q$ is the electronic charge, and $v(t)$ is the velocity of the charge carriers:

$$j(t) \propto \int I(t - t')[n(t')qv(t')]dt'. \quad (1.2)$$
1.3. THz generation using femtosecond laser pulses

The THz radiation properties like intensity and the bandwidth are determined mainly by the charge carrier lifetime, band-gap energy and resistivity of the material. A model of THz generation based on the Drude-Lorentz theory of a photoconductive antenna can be found in Refs. [30] and [31].

1.3.2 Optical rectification

THz pulses can also be generated by optical rectification of fs laser pulses in a medium with a strong second-order optical nonlinearity. Optical rectification of femtosecond pulses can be described using the concept of difference-frequency generation, which is a second-order nonlinear-optical phenomenon. The second-order nonlinear-optical polarization created in this manner is, in a simplified manner, given by [32]:

$$P^{(2)}(\Delta \omega) = \chi^{(2)} \int E(\omega_1)E^*(\omega_1 - \Delta \omega)d\omega_1,$$

where $\chi^{(2)}$ is the second-order susceptibility assumed to be frequency independent, and both frequencies $\omega_1$ and $\omega_1 - \Delta \omega$ involved in the process are assumed to come from the same laser pulse. The spectral components within the single femtosecond pulse spectrum are sufficiently apart such that the difference frequency of these components is in the THz domain. It can be shown that in the time domain and in the far field[33], the THz electric field is proportional to the second time derivative of the second-order nonlinear polarization induced by the laser pulse: $E_{THz} \propto \frac{\partial^2 P}{\partial t^2}$, with $P(t) \propto I(t)$, the intensity envelope of the laser pulse. This is illustrated in Fig. 1.3.
1.3.3 Current surge on semiconductor surfaces

In section 1.3.1, we described the THz emission through the acceleration of charge carriers in an externally applied electric field. Generation of THz radiation can also occur with the help of the electric field inherently present at the surfaces of semiconductors. The covalent bonds of the atoms in a semiconductor are broken at the surface, resulting in ‘dangling’ bonds. This is the cause of the formation of the so-called ‘surface states’. The surface states can act as donors or acceptors, causing the Fermi level of the semiconductor to be ‘pinned’ to the surface state energy. This is the origin of the built-in surface electric field, normal to the surface. The formation of the surface depletion field is illustrated in Fig. 1.4, for a p-type semiconductor [34].

When such a semiconductor surface is irradiated with femtosecond laser pulses, charge carriers are generated, which accelerate in the surface depletion field. In case of a p-type semiconductor, the electrons accelerate to the surface and the holes move towards the bulk of the semiconductor. This current surge gives rise to the emission of THz pulses according to Eq. 1.1 [11].

Another mechanism by which THz emission can occur is the ‘photo-Dember’ effect [35, 36]. Although this is also a surface-induced effect, the origin is the difference in mobilities of the electrons and holes. In other words, the
1.4. Plasmonics

The word plasmonics refers to the field of study related to surface-plasmons. Surface plasmons are electron density oscillations propagating along a metal surface, along with associated electromagnetic waves. An important property of surface plasmons is their surface-confined nature, resulting in the localization of the electromagnetic energy in very small volumes. In the work described in this thesis, we apply this localization of light in enhancing the

![Figure 1.4: Illustration of the band-bending and formation of a depletion layer at the surface of a p-type semiconductor. The vertical axis shows the energy. $E_c$ and $E_v$ denotes the conduction band and the valence band energy levels respectively. If laser pulses are incident on such a semiconductor, the photo-generated carriers are swept across the surface depletion field, generating a transient current. The arrows denote the direction in which the photo generated electrons and holes would accelerate. [34]](image-url)

electrons and holes generated by the optical pulses in the semiconductor have different diffusion velocities, resulting in a dipole perpendicular to the semiconductor surface. The photo-Dember effect has been shown to be an important contribution to the THz emission from a number of semiconductors like InAs [37], InSb [38], GaAs [39], GaSb [40], etc.

THz radiation can also be generated from the semiconductor surfaces by optical rectification (outlined in section 1.3.2), which is possible because at surfaces, the inversion symmetry is broken [41, 32]. In some materials, optical rectification, as well as depletion-field driven currents, have been shown to contribute towards THz generation [42, 43].
THz emission from metal surfaces (Chapter 2) and metal/semiconductor thin film interfaces (Chapter 5).

The first observation of surface plasmons was made in the year 1902, when Wood [44] reported an anomalous decrease of intensity at certain wavelengths in the spectrum of light reflected by a metallic grating, although he could not give an explanation for this phenomenon. He also noted that the sudden decrease in the reflection at certain wavelengths occurred only for p-polarized incident light, when the grating lines were oriented parallel to the magnetic field of the incident light. Rayleigh noticed that the anomalies in the spectrum of light reflected from a metal grating occur at the wavelength for which a scattered wave emerges tangentially to the grating surface [45]. He called these orders as “passing-off orders”, to show that an anomaly in the reflection spectrum occurs at a wavelength for which a higher order (1st, 2nd etc.) disappears at an angle parallel to the grating surface. This results in the re-arrangement of the intensities in the lower-diffraction orders. Now it is understood that these anomalies occur due to the excitation of surface plasmons by the periodic structure of the grating\(^1\). The dispersion relation of surface plasmons on metallic films was first theoretically derived by Ritchie [47] in 1957. His theory was proven to be valid through the experiments done by Powell and Swan [48], by measuring the electron energy loss spectra of Al foils. In 1968, Otto [49], as well as Kretschmann and Raether [50] demonstrated optical methods for exciting plasmons using prisms. In this technique, a glass prism is coated with a metal thin film. Light is incident on the metal coated surface through the glass side at a suitable angle, which excites surface plasmon resonances (SPR) at the metal/air interface. A review of the development of the field of plasmonics can be found in Ref. [51].

Nowadays, the field of plasmonics has expanded vastly, with applications spreading into chemical and biological sciences. Plasmon excitation using prisms is extremely sensitive to various changes at the metal surfaces and is now used as an indispensable tool for sensing biomolecules, called the SPR sensor [52]. An important potential use of plasmons is in enabling sub-wavelength photonic circuits [53]. Research has been going on in the past decade to study components of surface plasmon nano-photonics, such as splitters [54], waveguides [55], resonators [56], interferometers [57] etc. The strong local electromagnetic fields associated with the surface plasmons can also enhance various optical processes [58, 59]. This field enhancement property of surface plasmons has been exploited to improve the performance

\(^1\)An interesting article about the Wood’s anomalies can be found in [46].
of sensors [60], detectors [61, 62] and solar cells [63, 64], and several surface enhanced non-linear phenomena, like second harmonic generation, Raman spectroscopy, etc. [65, 66, 67].

Welsh et al. [68] demonstrated in 2007 that exciting surface plasmons using femtosecond laser pulses on shallow metal gratings can cause THz emission. It has been shown that random, as well as ordered metal nano-structures of gold can emit THz radiation due to the excitation of localized surface plasmons [69, 70]. Emission of terahertz radiation is also observed when surface plasmons are excited on a thin film of gold, in the Kretschmann geometry [71]. The THz emission from known THz emitters can also be enhanced in this manner. Most recently, plasmonic photoconductive antennas have been shown to enhance the terahertz emission compared to conventional photoconductive antennas [72, 73]. In these papers, interleaved plasmonic electrodes were used in order to reduce the transit time of the generated carriers to the electrodes.

1.5 This thesis

The goal of this thesis is to apply the field localization properties of surface plasmons to enhance the THz generation from metal/semiconductor Schottky-interfaces. In particular, the THz generation from Au/Cu$_2$O interfaces upon illumination with fs laser pulses is studied. The fabrication of the Cu$_2$O thin films used for the THz generation involves the oxidation of Cu thin films.

In Chapter 2, we introduce the concepts of surface plasmons and the excitation of surface plasmons on metal surfaces using gratings. The THz emission from thin gold films deposited on etched Si gratings, upon illumination with femtosecond laser pulses, is discussed.

Chapter 3 discusses the use of THz time-domain spectroscopy to study the oxidation of such ultra-thin Cu thin films deposited on Si substrates. The transmission of broadband THz pulses from 1 to 7 THz through the copper film is measured while it gets oxidized at an elevated temperature in ambient air. The change in the transmitted THz electric field is correlated with the growth of the cuprous oxide layer and the decrease in thickness of the copper layer.

In Chapter 4, we provide an overview of the THz generation experiments performed on Au/Cu$_2$O thin films. In this chapter, techniques like ellipsometry, x-ray diffraction, etc. are used to characterize the Au/Cu$_2$O interface.
In Chapter 5, we demonstrate the enhancement of THz generation from Au/Cu$_2$O interfaces using surface plasmon excitation. Gratings of suitable periodicity are used for the excitation of the surface plasmons. A systematic study of the dependence of the THz emission on the grating periodicity, azimuthal angle, oxide thickness etc. is carried out, to understand the role of surface plasmons in the emission enhancement. White light reflection spectroscopy measurements are also discussed, to give more information on the plasmon excitation.
2.1 Introduction to plasmonics

Surface plasmons are collective oscillations in the electron density on the surface of a metal. These surface charge oscillations, along with the associated electromagnetic waves, are called surface-plasmon polaritons\(^1\). The surface plasmons are strictly confined to the metal surface and the strength of the electric field decays exponentially away from the metal surface in both directions. A schematic representation of the surface charge density and the electric field of the surface plasmon polariton is shown in Fig. 2.1. The confined nature of surface plasmon polaritons makes it possible to concentrate light in sub-wavelength volumes, which may lead to large electric field enhancements [58, 59]. This field enhancement can effectively enhance several linear and nonlinear optical processes like second harmonic generation, SERS, fluorescence, absorption, etc. [59, 65, 66]. The field enhancement property of plasmons have also been used to increase the performance of devices like detectors, sensors, and solar cells [61, 60]. In this chapter, we will discuss the use of plasmonic nano-gratings to enhance the THz emission from thin gold films, when illuminated with ultra-short laser pulses. We investigate the importance of plasmon excitation in the THz generation with pump-power dependence and azimuthal-angle dependence measurements of the electric field of the emitted THz pulses. The mechanism of THz generation is also investigated.

\(^1\)In the literature the term ‘surface plasmon’ is also used to imply the electromagnetic waves associated with the charge density oscillations.
2.1.1 Dispersion relation of surface plasmons

Surface plasmons are characterized by the solutions of Maxwell’s equations that are localized at the interface of a metal and dielectric. If we consider the waves that propagate in the $x$ direction (see Fig. 2.1), it is possible to solve the wave equation to get a propagating transverse magnetic (TM) mode (for the derivation see Appendix. A). The electric field of the surface plasmons can be described as

$$E_j = (E_j,x, 0, E_j,z) e^{+i(k_jx \pm k_{j,z} z - \omega t)} \quad j = 1, 2,$$

where $j = 1, 2$ represents the dielectric and the metal, respectively. The $z$-component of the wave-vector, $k_{j,z}$, is imaginary, which causes the electric field to decay exponentially in the $z$-direction. $k_x$ is the $x$-component of the surface plasmon wave-vector, the component parallel to the interface. Solving Maxwell’s equations, with appropriate boundary conditions, it is possible to derive the dispersion relation of surface-plasmons as [74, 75]:

$$k_x = \frac{\omega}{c} \sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}},$$

where, $\epsilon_1$ and $\epsilon_2$ are the permittivities of the dielectric and the metal respectively, and $\omega$ is the angular frequency.
Let us assume, for convenience, that the imaginary parts of $\epsilon_1$ and $\epsilon_2$ are small compared to their real parts and can hence be neglected. To have waves which propagate along the interface, we need $k_x$ to be real. From Eq. 2.2, this condition is satisfied if the sum and product of the dielectric functions are either both positive or both negative.

Also, the normal component of the wave vector in both media is

$$k_{j,z} = \frac{\omega}{c} \sqrt{\frac{\epsilon_j^2}{\epsilon_1 + \epsilon_2}}, \quad j = 1, 2. \quad (2.3)$$

Since the wave is confined to the interface, $k_z$ has to be purely imaginary in both media, such that the electric field is exponentially decaying away from the interface. This requires the sum of the dielectric functions to be negative, as can be seen from Eq. 2.3. Hence, the condition to have waves confined to the interface becomes

$$\epsilon_1(\omega)\epsilon_2(\omega) < 0, \quad (2.4)$$

and

$$\epsilon_1(\omega) + \epsilon_2(\omega) < 0. \quad (2.5)$$

For the above two conditions to be satisfied simultaneously, only one of the dielectric functions has to be negative and its absolute value should be greater than that of the other. The real-part of the permittivity of metals is usually negative with a large value compared to the absolute value of the permittivity of dielectrics. This explains why surface plasmons are possible at the interface between a metal and a dielectric.

In the above discussion, we considered the permittivities of the two media to be real, which helps to understand why a metal/dielectric interface is necessary for the excitation of surface plasmons. However, in reality, both the materials forming the interface can also have an imaginary part of the dielectric function. This leads to $k_x$ having an imaginary part as well, leading to the damping of surface plasmons propagating along the interface, which is explained in the next section.

### 2.1.2 Properties of surface plasmons

The properties of surface plasmons are well known and are summarized here for convenience, following the derivation of Novotny and Hecht [75].
Let us assume that the complex permittivity of the metal is

\[ \epsilon_2 = \epsilon'_2 + i\epsilon''_2, \]  

(2.6)

where \( \epsilon'_2 \) and \( \epsilon''_2 \) are real. The permittivity of the dielectric \( \epsilon_1 \) is assumed to be real for simplicity. The real and imaginary parts of \( k_x \) can then be obtained from Eq. 2.2 as [75]

\[ k'_x \approx \sqrt{\frac{\epsilon'_2\epsilon_1}{\epsilon'_2 + \epsilon_1}} \frac{\omega}{c}, \]  

(2.7)

and

\[ k''_x \approx \sqrt{\frac{\epsilon'_2\epsilon_1}{\epsilon'_2 + \epsilon_1}} \frac{\epsilon''_2\epsilon_1}{2\epsilon'_2(\epsilon'_2 + \epsilon_1)} \frac{\omega}{c}. \]  

(2.8)

The wavelength of the surface plasmon can be obtained from the real part \( k'_x \) as

\[ \lambda_{\text{SPP}} = \frac{2\pi}{k'_x} \approx \sqrt{\frac{\epsilon'_2 + \epsilon_1}{\epsilon'_2\epsilon_1}} \lambda, \]  

(2.9)

where \( \lambda \) is the excitation wavelength in vacuum.

The imaginary part \( k''_x \) accounts for the damping of the surface plasmon as it propagates along the interface. The damping of the surface plasmons occurs due to the ohmic losses of the electrons participating in the surface plasmon oscillations and finally results in the heating of the metal.

The 1/e decay lengths of the electric field in the z-direction (direction perpendicular to the interface) in both the materials can be obtained by calculating the respective value of \( 1/k_{j,z} \). When the metal has a complex permittivity, the value of the propagation constant of the SPP electric fields in the metal and in the dielectric can be obtained from Eq. 2.3 as

\[ k_{2,z} = \frac{\omega}{c} \sqrt{\frac{\epsilon'_2^2}{\epsilon'_2 + \epsilon_1}[1 + i\frac{\epsilon''_2}{2\epsilon'_2}]}, \]  

(2.10)

and

\[ k_{1,z} = \frac{\omega}{c} \sqrt{\frac{\epsilon'_1}{\epsilon'_2 + \epsilon_1}[1 - i\frac{\epsilon''_2}{2(\epsilon'_2 + \epsilon_1)}]} \]  

(2.11)
2.2 Grating coupling of surface plasmons

The dispersion relation of surface plasmons at a metal/dielectric interface, is plotted schematically in Fig. 2.2. The solid black line represents the dispersion relation given in Eq. 2.2, where for simplicity and illustration purposes, we have used only the real part of the dielectric permittivity of the metal. It has two branches. The high frequency branch does not represent true surface waves, since $k_z$ is not purely imaginary here. The surface plasmon dispersion relation is represented by the low energy branch and we will consider only this branch further in our discussions.\(^2\)

The dashed line represents the light line in air, $\omega = ck_x$, propagating in the x-direction. As can be seen from the figure, at a given frequency of the incident light $\omega_{inc}$, the wave-vector $k_{SPP}$ of the plasmon is always greater than the wave vector of light in free space, $k_{inc,x}$. Hence, to excite surface plasmons using light we have to increase its wavevector from its free space value. There are several ways to achieve this.

One of the methods is to excite surface plasmons using evanescent waves created at the interface of a medium of refractive index $n$ greater than 1. This is usually achieved using prisms, either in the Otto, or in the Kretschmann configuration [74]. Another method to excite surface plasmons is to use gratings, which is the technique we describe in this chapter. A grating is a periodic structure that has a fixed periodicity and a fixed wave-vector that can be added (or subtracted) from the incident light wave-vector. The wave-vector of the grating is given by,

$$k_g = \frac{2\pi}{\Lambda},$$

(2.12)

where $\Lambda$ is the periodicity of the grating. If $\theta$ is the angle of the incident light with respect to the surface normal, the wave vector of the light that gets diffracted by the grating can have components along the surface ($\frac{\omega}{c}$) $\sin \theta \pm Nk_g$, where $N = 1, 2, 3, ...$ The plasmon excitation condition now becomes:

$$\frac{\omega}{c} \sin \theta \pm N\frac{2\pi}{\Lambda} = k_{SPP} = \frac{\omega}{c} \sqrt{\frac{\epsilon_1\epsilon_2}{\epsilon_1 + \epsilon_2}},$$

(2.13)

where $k_{SPP}$ is the wave-vector of the surface plasmon.

A schematic illustration of the coupling of surface plasmons using gratings is shown in Fig. 2.3. The red lines represent the dispersion of the

\(^2\)If the complex permittivity of the metal is considered, there is a continuous transition from the lower plasmon branch to the upper branch.
surface plasmon polaritons propagating in the forward and the backward x-directions along a metal surface. The blue lines represent the boundaries of the brillouin zones in k-space due to the scattering by the grating, corresponding to \( N = \pm 1 \). Higher values of \( N \) are not represented in the picture for simplicity. The grey, dashed line shows the dispersion curve of the incident light in vacuum. The resultant dispersion line when the grating vector is added to/subtracted from the incident light is represented by the grey solid lines. It can be seen that the incident light dispersion, when added to/subtracted from the grating vector satisfies the surface plasmon excitation condition at two frequencies \( \omega_{+1} \) and \( \omega_{-1} \). If the light is normally incident on the grating and thus \( k_{inc,x} = 0 \), the plasmons, propagating in both positive and negative directions along the x-axis, can be excited at a single frequency. This frequency is defined by where the vertical lines at \( k = k_g \) and \( k = -k_g \) cross the plasmon dispersion curve. If the angle of incidence is not 90°, for a fixed frequency only one plasmon can be excited. However, in principle, two counter-propagating plasmons are possible, but only by excitation using two different frequencies, \( \omega_1 \) and \( \omega_2 \). Considering an angle of incidence in between 0° and 90°, the direction of propagation...
2.2. Grating coupling of surface plasmons

Figure 2.3: (a) The grating coupling of surface plasmons is illustrated. The x-component of the incident light ($k_{\text{inc},x}$) is shown by the dashed grey line. The scattering of the incident light by the grating results in the lines $k_{\text{inc},x} + k_g$ and $k_{\text{inc},x} - k_g$. Only the first-order diffracted light is shown here, for simplicity. Plasmons are excited for the frequencies where these lines intersect with the plasmon dispersion lines $k_{\text{SPP}}$ and $-k_{\text{SPP}}$. From the figure it can be seen that surface plasmons can be excited for two frequencies $\omega + \omega_1$ and $\omega - \omega_1$. (b) and (c) show the direction of propagation of the surface plasmons for the two excitation light frequencies $\omega - \omega_1$ and $\omega + \omega_1$ respectively. $\theta$ is the angle of incidence of the exciting light with respect to the normal to the metal surface.

of the surface plasmons for the two cases is schematically shown in Fig. 2.3 (b) and (c).
2.2.1 Plasmon excitation with a metal grating for non-zero azimuthal angles

The azimuthal angle $\phi$ is defined as the angle between the grating vector and the plane of incidence of the excitation laser beam, as shown in Fig. 2.4. The plasmon coupling condition given in Eq. 2.13 is valid only for the case when $\phi = 0$. For non-zero azimuthal angles, the grating vector, the plasmon vector, and the $k$-vector component of the incident light in the plane of the grating are not collinear. Hence, the surface plasmon coupling condition becomes [76]

$$k_{\text{SPP}}^2 = k_0^2 \sin^2 \theta + N^2 k_g^2 \pm 2N k_g k_0 \sin \theta \cos \phi,$$  \hspace{1cm} (2.14)

where $\theta$ is the angle of incidence of the light beam and $\phi$ is the azimuthal angle (see Fig. 2.4). Now, plasmon excitation is possible if the vector addition of the grating vector and the incident light matches with the surface plasmon wave vector. A schematic diagram of the plasmon excitation condition is shown in the Fig. 2.4, where light incident at a polar angle $\theta$ and an azimuthal angle $\phi$ can couple to a grating of wave vector $k_g$. The angle $\Psi$ between the direction of propagation of the resulting surface plasmon...
with respect to the in-plane component of the incident vector, is given as

\[ \Psi = 90 - \arccos\left( \frac{k_g \sin \phi}{k_{SPP}} \right) \]  

(2.15)

### 2.3 THz emission from gold thin films - a literature survey

In this section, we discuss the generation of THz radiation from gold-coated grating surfaces, upon fs pulse irradiation and subsequent surface plasmon excitation. There have been several reports in the literature of THz emission from Au thin films. There are various non-linear optical processes which may lead to the generation of THz light from these metal films, depending on the experimental conditions, like incident power density, morphology of the metal film, etc. Below, we describe briefly the various cases of THz generation from metal thin films, as reported previously in the literature.

#### 2.3.1 Optical rectification

Optical rectification on metal surfaces like gold and silver, was first reported by Kadlec et al. [77] in 2004.\(^3\) This paper reported that when surfaces of gold and silver are irradiated with high energy laser pulses (1-mJ) of 810 nm center wavelength and 50 fs pulse duration, optical rectification of the laser pulses occurs at the metal surface, resulting in the generation of THz pulses. They observed the THz fluence emitted by the gold surfaces to be proportional to the square of the pump laser fluence.

Second-order non-linear optical effects like optical rectification require materials that lack inversion symmetry. Metals are mostly isotropic materials and, hence, optical rectification cannot take place in the interior of metals. However, at the surface, the translational symmetry is broken, allowing \(\chi^{(2)}\) nonlinear effects like second harmonic generation [79, 80] to take place. Hence, it was concluded that optical rectification on the metal surface is the terahertz emission mechanism. In another paper, Kadlec et al. [81] also noted that the THz emission depends on the thickness of the gold thin film, and no THz emission was observed for film thicknesses less than 100 nm.

\(^3\)At the same time, Hilton et al. [78] also reported THz emission from single-crystal thin iron films by optical rectification. The THz emission was explained as arising from a magnetic nonlinearity in addition to the surface nonlinearity of the thin film sample.
This was explained in the paper as follows: The nonlinear polarization at the surface induces a current perpendicular to the metal surface and, for thin Au films, the charges can accumulate on the metal-glass interface, resulting in the rapid build up of a field opposing the initial current that is the origin of the THz emission.

However, Ramakrishnan and Planken [69] reported THz emission from ultra-thin layers of Au on glass substrates, with thicknesses much lower than that used by Kadlec et al. [77]. The Au layer films of thicknesses as low as 10 nm were reported to emit THz radiation upon illumination with fs laser pulses, based on a second-order nonlinear optical process. They reported that the THz emission is enhanced since the evaporated thin films of such low thicknesses do not form a continuous Au layer on the surface, but a random, percolating structure. The THz emission was reported in the paper to be the maximum just above the percolation threshold. The reason for enhanced emission is the excitation of localized surface-plasmon intensity hot spots in the percolated metallic thin film, resulting in enhanced fields and in enhanced optical rectification of the incident femtosecond laser pulses. The emitting dipole was assumed to be perpendicular to the surface, since the polarity of the THz emission was found to change sign while changing the angle of incidence from +45° to -45° (See Fig. 2.5).

Ramakrishnan et al. [71] also reported in 2012 that thicker, continuous flat gold films irradiated with fs laser pulses also emit THz radiation, when surface plasmons are excited in the Kretschmann geometry. Apart from thin Au films, surface immobilized gold nano-spheres (SIGNs) above a gold surface were also observed to emit THz radiation originating from optical rectification, as reported by Kajikawa et al. [82].

### 2.3.2 Multiphoton excitation

THz emission from Au films may also occur through a photo-emission process, where electrons are emitted from a material by the absorption of photons. The energy needed to eject an electron out of the Au surface is around 5.3 eV. The photon energy of light having a wavelength of 800 nm is around 1.5 eV. Hence, photoemission can occur from the metal surface through a multi-photon photoelectric effect at this laser wavelength. It has been shown that surface plasmons excited by femtosecond laser pulses are capable of inducing multi-photon excitation of electrons in metals in vacuum [83]. The free electrons (excited from metal into air) near the surface of the metal experience a ‘ponderomotive force’ [84], which is the force experienced by a charged particle in a non-uniform oscillating electromagnetic
2.3. THz emission from gold thin films - a literature survey

Figure 2.5: The THz pulses emitted by a 8 nm percolating Au thin film on a glass substrate, for angles of incidence $+45^\circ$ and $-45^\circ$, as reported by Ramakrishnan and Planken [69]. The measurement was done in a transmission configuration, with the pump light incident on the glass side of the sample. No THz emission was detected at normal incidence.

field. The free electrons near the metal are accelerated towards the region of lower electric field strength, which, in the case of the evanescent field of surface plasmons, is away from the metal surface.

THz generation from Au thin films, attributed to the mechanism described above, was first proposed in 2007, by Welsh and Wynne [85]. They employed gold gratings to excite surface plasmons with ultrafast laser pulses, and generated pulses of terahertz radiation. THz emission was observed when the angle of incidence of the pump laser pulse on the metal grating was suitable for excitation of surface plasmons [68]. In their experiments an amplified laser was used generating pulses with an energy of 1-mJ, wavelength 800 nm and a duration of 100 fs. The dependence of the THz fluence on incident laser power showed a power-law dependence $I_{THz} \propto I_{pump}^{3.5}$, suggestive of a multi-photon photoelectric effect as a cause of the THz generation. Since the work function of gold is around 5.3 eV, at least 4 photons are required for multi-photon excitation when exciting with a laser of photon energy 1.5 eV. However, the effective order of the process can be reduced at higher pump intensities [85], due to the modification of the potential by the laser field and the resulting tunneling of photoelectrons out of the metal [86].
In 2009, Gao et al. [87] theoretically investigated the plasmon-based photoemission model from gold nanostructures. They showed that the electric field inside the metal is an important factor on which the number of electrons emitted, and hence the strength of the THz electric field depends. Hence, the design of the nanostructure can play an important role in the generation of THz pulses. Polyushkin et al. [70] later demonstrated THz emission from arrays of silver nano-particles irradiated by strong femtosecond laser pulses. The THz emission intensity in their experiments depends on the pump intensity as $I_{\text{pump}}^5$, for incident power intensities less than 5 GW/cm$^2$ and drops to a 1.5 - 1.75 order power dependence for higher pump power intensities. This bimodal power dependence is consistent with the model based on ponderomotive acceleration of the photo-generated electrons, since ultrafast photo-emission measurements have also shown such bimodal power dependencies [88]. The handwaving explanation given by the authors is that at low incident power densities, the ponderomotive potential is not completely converted into kinetic energy of the electrons before the lifetime of the plasmon pulse. If the incident power density is higher, the electrons are pushed out of the field within the lifetime of the plasmons and the transfer of energy from ponderomotive potential to the kinetic energy of electrons is more significant [83].

### 2.3.3 Other mechanisms

It is interesting that various groups have reported THz emission from metal surfaces and nano-structures, but that the reported dependence of the emitted THz electric field on pump power, varies. In addition to the second-order and higher-order pump power dependencies of the emitted THz electric field explained briefly in the previous sections, Garwe et al. [89] reported a linear dependence of emitted THz fluence on the pump laser fluence. This contradicts the model assumed by Welsh and Wynne [85] and Polyushkin et al. [70], based on the ponderomotive acceleration of photo-emitted electrons, which can occur only through a higher-order process. To explain their observations, they (Garwe et al. [89]) consider a model where surface plasmon polaritons propagate perpendicular to the grooves of the gold grating surface, constituting a transient current, which emits THz pulses directly [90]. However, creation of photons of a different color requires at least a second-order nonlinear process, which leads to at least a quadratic dependence of THz fluence on the laser power. This makes the linear power dependence observed in their experiments a bit puzzling. An interesting aspect of the experimental setup used by Garwe et al. [89] is that they used
2.4. THz emission from gold gratings

Inspired by the various mechanisms suggested in literature as being responsible for the emission of THz light from metal surfaces illuminated with femtosecond laser pulses, we performed THz emission experiments with plasmonic metal gratings. Our goal is to determine the role played by surface plasmons in the THz generation. Initial experiments were performed using a commercially obtained etched grating on quartz, similar to that used by Welsh et al. [68]. The periodicity of the grating is 500 nm. We deposited a thin layer of Cr (2 nm) with a Au layer of 40 nm thickness on top. The Cr layer is to promote the adhesion between the Au and the quartz substrate. From the plasmon-excitation condition given in Eq. 2.13, we can calculate that for this periodicity, a plasmon resonance should appear at an angle of 36°.

To confirm that we can excite plasmons on this grating, we have performed white-light transmission spectroscopy measurements. An Ocean Optics fiber-coupled spectrometer was used to measure the spectral transmission using a Tungsten-Halogen lamp as a white-light source. The transmission spectra of the light through the grating sample were measured for different angles of incidence. The measurements are normalized to the transmission through a flat gold film of equal thickness on the glass substrate. The experimental transmission spectra thus obtained are shown in Fig. 2.6. We see peaks in the transmission through the Au grating compared to the flat gold film, with the peak wavelength depending on the angle of incidence. This increased transmission efficiency has been attributed to the excitation of surface plasmons [93, 94]. At an angle of incidence of 36°, a resonance


Figure 2.6: The transmission spectra of the 500 nm periodicity gold grating on a glass substrate, for four different angles of incidence. The transmission spectra are normalized to the transmission spectrum of a flat gold film, at the same angle of incidence. The peaks correspond to plasmon excitation and the plasmon resonance wavelength is dependent on the angle of incidence.

is observed at a wavelength of 800 nm, confirming the excitation of surface plasmons in the THz generation experiment.

The experimental setup used for the THz generation and detection is shown in Fig. 2.7 (a). The laser source used in the experiments described in this chapter is a Ti:Sapphire oscillator with an average power of 800 mW, 50 fs pulse duration and a center wavelength of 800 nm. The repetition rate of the laser pulses is 11 MHz. The laser beam was split into two using a 90:10 beam splitter. The stronger beam is used as the pump beam to generate THz pulses and the weaker beam is used to probe the THz electric field at the detection crystal. The pump beam is brought to be incident on the Au grating sample at an angle of 36°, the angle at which we expect plasmon excitation to take place. The generated THz pulses are collected in the reflection direction and collimated using a parabolic mirror. Another parabolic mirror focuses the generated THz radiation onto an electro-optic (110) ZnTe crystal of 500 µm thickness. The probe beam is also focused onto the ZnTe crystal through an aperture in the second parabolic mirror.
2.4. THz emission from gold gratings

![Diagram of experimental setup](image)

**Figure 2.7:** (a) Experimental setup used for the generation and detection of THz light from gold gratings using plasmon excitation. (b) Schematic diagram of the sample and the measurement configuration. (c) THz emission from a metal grating illuminated at an angle of 36° in the reflection configuration. (d) Pump power dependence of THz emission from the gold grating sample.

The polarization of the probe beam is modified by the electric field of the THz pulse inside the ZnTe crystal. The change in polarization of the pump beam is measured using a combination of a quarter-wave plate, a Wollaston prism and a differential detector.

In Fig. 2.7 (c), we show the time-dependent electric field of the THz pulse emitted from the Au grating, when illuminated with 800 nm laser pulses at an angle of 36°. In red is the pulse emitted when the metal grating grooves are oriented perpendicular to the p-polarized incident laser pulses, corresponding to an azimuthal angle φ = 0°. When φ = 90°, we do not observe any THz emission, as shown by the black curve. We also measured the pump power dependence of the THz emission from the Au grating. Fig. 2.7 (d) shows the measured electric-field amplitude of the THz pulses.
2.4.1 Azimuthal-angle dependence

The dependence of the pump power absorption on the azimuthal angle was also measured. The absorption of the pump laser was obtained by measuring the percentage of the reflected as well as the transmitted power, as shown in Fig. 2.8(a). In Fig. 2.8 (b), the blue line shows the percentage emitted vs. the input pump power (black dots). The solid line is a fit to the measured data. The straight line fit to the data indicates a second-order non-linearity as the source of the THz emission.
of the laser power absorbed as a function of the azimuthal angle. For efficient plasmon excitation to take place, the grating grooves should be oriented perpendicular to the laser polarization and, hence, when $\phi = 0^\circ$, we observe a peak in the absorption. The THz emission is correlated with the absorbed laser power (see Fig. 2.8(b)): the amplitude of the emitted THz pulse also sharply decreases as the azimuthal angle is changed from $0^\circ$, and at $90^\circ$, there is no detectable THz emission.

Here we see that a relatively small increase in absorbed power leads to a big change in the THz amplitude. This demonstrates that it is not enough to simply increase the absorption, but that plasmon excitation is very important for the THz emission.

### 2.5 Etch depth dependence

Since it is easier to perform the experiment for an angle of incidence of $45^\circ$, we also fabricated gratings with a periodicity suitable for plasmon excitation at $45^\circ$. Such a grating should have a periodicity of $\sim 463$ nm. We fabricated these gratings using electron-beam lithography and reactive ion etching. The gratings were first etched into silicon substrates and then covered with Au by evaporation. The thickness of the Au layer is 100 nm and an adhesive Cr layer of 10 nm thickness was evaporated before Au.

Since these gratings are fabricated on Si, which does not transmit any light below $\sim 1100$ nm, and also because the Au layer is 100 nm thick, transmission spectra could not be obtained for these samples. In Fig. 2.9 (a) we show the visible light reflection spectra of the fabricated Au nano-gratings of periodicity 463 nm. The gratings have etch-depths varying from 20 nm to 60 nm. The spectra are normalized to the reflection spectrum of a bare Au surface. It can be seen that around a wavelength of 800 nm, a plasmonic resonance appears. The strength of the resonance depends on the etch depth and is largest for an etch depth of 60 nm. Around $\lambda = 787$ nm, there is a discontinuity in the reflection spectrum, which correspond to Wood’s anomaly [46]. Below this wavelength, the diffracted order corresponding to $N = -1$ disappears and hence the energy is redistributed to the zeroth order. We see that the difference of intensity before and after the Wood’s anomaly discontinuity increases with the etch depth. This is because the diffraction intensity depends on the etch depth of the grating [74].

The THz emission from these gratings was recorded in a reflection configuration with an angle of incidence of $45^\circ$ of the pump laser pulses. The
Figure 2.9: (a) Reflection spectra from gold-gratings of periodicity 463 nm for four different etch depths at 45° angle of incidence. (b) THz pulses emitted by the gold-gratings upon excitation with p-polarized femtosecond laser pulses. No THz emission was observed from the grating with an etch depth of 20 nm.
measured electric field of the emitted THz pulses is plotted in Fig. 2.9 (b). The maximum THz emission is observed for a sample with an etch depth of 60 nm. The strongest plasmon resonance at the pump laser wavelength was also observed for this grating etch-depth, again providing support for the idea that plasmon excitation is necessary for the THz emission.

2.6 Discussion

Mainly two types of explanations have been given in literature to explain the THz emission from Au thin films and surfaces: one based on photoemission from the Au surface [70, 68, 85] and the other based on a surface nonlinearity [77, 81, 82, 71, 69]. THz emission seen after plasmon excitation on gratings and nano-particles, was observed to have a higher-order pump-power dependence and hence could be explained as originating from multi-photon excitation of electrons and subsequent acceleration in the evanescent field of the surface plasmons [68, 70]. However, in our experiments, a second-order dependence on the pump power is observed (Fig. 2.7(d)). As mentioned in section 2.3, a multi-photon excitation cannot be a second-order process, since the energy of the 800 nm photon is at least 4 times less than the work function of gold. Hence, multi-photon excitation can be ruled out as the THz generation mechanism. It is interesting that Welsh et al. [68] observe a higher-order dependence of the THz emission on incident laser power than we do, considering that we have used an identical grating. However, the laser power incident on the sample in our case is much lower than that used by Welsh et al. [68] and Polyushkin et al. [70]. Higher-order processes require a high pump power, which may be the reason why we do not observe it in our case. At the same time, Welsh et al. and Polyushkin et al. use a low repetition rate amplified laser which is not suitable to detect the weaker emission associated with a possible $\chi^{(2)}$ process. It is therefore possible that our experiment and those of Welsh et al. and Polyushkin et al. simply probe two different power regimes and two different THz generation mechanisms.

The second-order dependence of the generated THz power on the incident laser power suggests optical-rectification by the surface non-linearity as the source of the THz light. Using low power laser sources, a second-order THz generation process from gold thin films has been observed only for the case of percolated-gold by Ramakrishnan and Planken [69] using similar pump powers. The emitting THz dipole, in the case of percolated gold was assumed to be along the surface normal (see also Fig. 2.5). Moreover, the
generated THz pulses were found to be p-polarized, irrespective of whether the incident laser polarization was s or p.

In order to check the effect of having s-polarized incident light, we fabricated another grating of periodicity 1090 nm, suitable for exciting surface plasmons at an angle of incidence of 45° and an azimuthal angle of 90°. The white-light reflection spectra of this grating for different azimuthal angles, and s-polarized incident light, are shown in Fig. 2.10. It can be seen that the plasmon resonance wavelength depends strongly on the azimuthal angle. When \( \phi = 102° \), the plasmon resonances seen at \( \sim 700 \) nm and \( \sim 1 \) \( \mu \)m correspond to the plasmons excited through the grating vectors \( \pm k_g \). When \( \phi = 90° \), surface plasmons excited from both \( \pm k_g \) merge and both these plasmon modes seem to have almost the same frequency.

The THz pulse emitted from this sample oriented at an azimuthal angle of 90°, when excited with s-polarized pump laser pulses, is shown in Fig. 2.11. We measured both s- and p-polarized components in the generated THz pulse. The presence of an s-polarized component in the THz light cannot easily be explained on the basis of an emitting dipole along the surface normal. This would mean that the surface \( \chi^{(2)} \) of the sample is unlikely to be the only contributing THz generation mechanism.
2.6. Discussion

Another possible explanation for the THz emission which has not been explored very much, is the photon drag effect [95]. This is the effect by which the momentum of photons is transferred to the free charge carriers in the material in which the light propagates, creating a current [96]. Photon drag can also be interpreted as a dynamic Hall effect [97]. The electric and magnetic field of the incident light beam exerts a Lorentz force on the electrons, resulting in a polarization parallel to the light propagation direction. In metals, Vengurlekar and Ishihara [98] showed that the excitation of surface plasmons can enhance this photon-drag effect. Hatano et al. [99] studied the photo-induced voltage resulting from the photon drag effect in metal gratings. Kurosawa and Ishihara [100] also demonstrated that surface plasmons, excited using metal gratings, can drive the electrons in the metal in the direction of the surface plasmon. Since the momentum is imparted to the electrons via the surface plasmons, this effect is called surface-plasmon drag effect.

It has been theoretically demonstrated that ‘surface-plasmon-induced drag-effect rectification’ (SPIDER) in metal nano-wires [101] can generate THz pulses. It was shown in that paper that ultrashort and nanolocalized plasmon pulses exert a force on the electrons in the nano-wire, inducing a giant THz polarization in the plasmon propagation direction. In our grating sam-

\[ \begin{align*}
\text{Figure 2.11: THz emission from a metal grating of periodicity 1090 nm. The experimental conditions are: } \theta &= 45^\circ, \phi = 90^\circ, \text{ and the incident pump laser is s-polarized.}
\end{align*} \]
Figure 2.12: The directions of the two surface-plasmon modes that are excited when the grating is oriented at an azimuthal angle of $90^\circ$, are illustrated.

ple of periodicity 1090 nm, the surface plasmons are expected to travel at an angle of $\sim 46^\circ (\alpha$ in Fig. 2.12), with respect to the plane of the incident laser, along the surface of the grating. A plasmon-induced drag current in the direction of surface plasmons can be produced and the resulting THz pulse could thus have both s- and p-polarized components. The s-polarized light observed in Fig. 2.11 could thus be explained.

An argument against the photon drag effect being the reason for the THz emission is described below. The two surface plasmons excited at $\phi = 90^\circ$, are illustrated in Fig. 2.12. These plasmon wave-vectors have equal magnitudes and opposite directions for their y-components. In such a case, it seems unlikely that a photon drag current can exist in the y-direction since the emission from both directions would cancel, resulting in no THz generation. Another aspect which is not yet clear is the magnitude of the p-polarized THz pulse being smaller than the corresponding s-polarized THz pulses. We also note that for a sample with a grating periodicity of 1090 nm, the plasmon resonance is at 830 nm (at $\phi = 0^\circ$), which is not exactly at the laser wavelength 800 nm. Selective excitation of the plasmon propagating in only one direction can be achieved by suitable design of the grating periodicity for azimuthal angles different from 0 or $90^\circ$. This could probably help us to prove how much photon-drag currents contribute to the terahertz generation from these thin metal nano-gratings using plasmon excitation.
Chapter 3

Oxidation kinetics of Cu thin films

The work described in this chapter has been published in [102], and is largely reproduced here, with modifications.

3.1 Introduction

Copper and copper-based alloys are very popular for use in the electronics and optoelectronics industry because of their low cost, high thermal and electrical conductivity and ease of fabrication. For example, copper is preferred over aluminium in ultra large scale integration devices for use as an interconnect material because of its low electrical resistivity [103, 104]. Copper foils are also used as the conductive element in flexible circuits. However, the surface of copper easily oxidizes and the oxide layer formed does not provide enough protection to prevent further oxidation [105]. Oxidation is an important factor which degrades the performance of copper-based electronic devices [106].

Copper is also an important material for terahertz (THz) applications. Due to the high conductivity, copper can be used for metal wire and parallel plate THz waveguides [107, 108, 109] and for the production of sharp tips in aperture-less near field scanning optical microscopy [25]. The presence of even a thin oxide layer on a metal surface can, in principle, distort the propagation of THz surface waves [110]. This occurs because the surface wave propagates along the wire and interacts with this thin layer over a long propagation distance of several cm or more. Another interesting application of copper and in particular, one of the oxides of copper, cuprous oxide, is that in combination with a metal, the oxide/metal interface constitutes a surprisingly good THz emitter [92]. Hence, it is interesting to study the oxidation of copper and the effect it has on the THz optical properties.
of copper surfaces. In chapter 4, we also discuss the THz generation from Au/Cu$_2$O interfaces. For this purpose, the Cu$_2$O films are fabricated by oxidizing thin Cu films on Au substrates by heating in the ambient atmosphere. The study of oxidation of thin Cu films is important in this respect as well.

In the past, different techniques have been employed to measure the oxidation of copper and copper thin films [111, 112, 113, 114]. Njeh et al. [111] discuss the oxidation of copper thin films in air using x-ray reflectometry and x-ray diffraction at temperatures below 250 °C. Ellipsometry, using 350 nm to 850 nm light, has also been employed successfully to characterize the oxidation kinetics by Iijima et al. [112]. It was shown by Zhong et al. [113] that the measurement of the sheet resistance of copper layers during oxidation can also give information about the oxidation kinetics. In the latter technique, the change in sheet resistance was correlated with the thinning of the copper metal layer due to oxidation. Transmission electron microscopy has also been used to obtain insight into the initial stages of oxidation [114]. All these techniques, however, either provide little information on the optical properties of copper during the various stages of oxidation of a copper surface, or require physical contact to be made with the copper which may influence the measurement.

In this chapter, we explore a new method to study the oxidation of Cu films at elevated temperatures in the range of 120 to 150 °C in air by non-contact, in-situ transmission measurements of broadband terahertz pulses. We attempt to calibrate the transmission of THz light through thin Cu films, to extract the instantaneous thickness of the copper layer and the thickness of the Cu$_2$O layer during oxidation from the instantaneous THz transmission. This can give us more information on the oxidation kinetics and activation energy for oxidation.

### 3.2 THz transmission through oxidizing Cu thin films

We used a THz time-domain spectroscopy setup to measure the instantaneous transmission of the Cu thin films, while oxidizing them by heating in the ambient atmosphere. The details of the sample and the experimental setup are described below.
3.2. THz transmission through oxidizing Cu thin films

3.2.1 Experiment

The copper thin films were fabricated using electron-beam evaporation. The films were evaporated onto clean, high resistivity silicon substrates by an e-beam evaporator in a vacuum of $1 \times 10^{-4}$ Pa. The thickness of the evaporated thin films is measured using a quartz crystal resonator positioned inside the evaporation chamber. The evaporation rate used to prepare the samples was $1 \text{ Å/s}$. X-ray diffraction measurements of evaporated samples show that the evaporated Cu films are polycrystalline in nature.

To heat the copper film, the sample was sandwiched between two copper plates, connected to a soldering iron. A thermal paste was used to ensure a good thermal contact between the mount and the sample. To measure the temperature of the sample, we also inserted a thermocouple in a small space between the two copper plates. Using this arrangement, we are able to heat the sample at a specified temperature up to $250 \degree C$. For the THz transmission measurement, the heating mount with the sample is positioned at the focus of the THz beam. 3 mm diameter holes were drilled into the copper plates to allow transmission of the THz beam through the sample.

The experimental set-up used for our THz transmission measurements is schematically shown in Fig. 3.1. We use 50 fs laser pulses with a center wavelength of 800 nm from a Ti:Sapphire oscillator (Scientific XL, Femto-lasers, Vienna) with an average power of 2.5 W and a repetition rate of 5.2 MHz. The laser beam is split into a pump beam and a probe beam by a 90:10 beam splitter. The high power beam is used as the pump beam to generate single cycle THz pulses from a 300 μm thick (110) GaP crystal by
optical rectification. Optical rectification can be interpreted as difference frequency mixing of the frequencies within the bandwidth of the femtosecond laser pulses giving rise to the creation of THz photons. The generated THz pulses are collected, collimated and focussed onto the sample using two parabolic mirrors. Another two parabolic mirrors collect and focus the beam again onto another 300 µm GaP crystal which acts as electro-optic detection crystal [115, 116]. The probe beam is also focussed onto the electro-optic detection crystal through a hole in the last parabolic mirror. In the electro-optic crystal, the instantaneous electric field of the THz pulse elliptically polarizes the probe beam. The ellipticity induced in the probe beam is measured using a system of a quarter wave plate, a Wollaston prism, and a differential detector and is proportional to the instantaneous THz electric field. Since the detection efficiency also depends on the azimuthal angle of the crystal, the crystal is rotated around the surface normal to maximize the signal. The strongest detected signals are obtained when the angle between the 800 nm probe polarization and the THz polarization is either 90° or 0° [33]. The pump pulses and, hence, the THz pulses, are delayed using a retro-reflecting mirror arrangement mounted on a loudspeaker oscillating at 50 Hz. By varying the delay between the THz and probe pulses we can measure the THz electric field in a stroboscopic manner. In this way, we get a 25 ps long THz electric field time trace, every 20 ms [117].

3.2.2 Results

Fig. 3.2(a) shows the temporal waveform of a typical THz pulse detected after passing through a 9 nm thick copper film on a thick silicon wafer. For reference, the THz pulse detected after passing through an uncoated silicon wafer is also shown. The detected THz electric field consists of almost a single cycle. The rapidly oscillating tail following the main pulse is due to the phase mismatch between the pump laser pulses and the THz pulses in the generation crystal [115]. By performing a fast fourier transform of the temporal data, we obtain the amplitude spectra of the pulses as shown in Fig. 3.2(b). The ultrafast THz pulses are seen to contain usable spectral components in a wide bandwidth from 0.5 to 7 THz.

Fig. 3.3 shows the normalized peak-to-peak value of the electric field of the THz pulses transmitted through the copper films, as a function of time. The films were heated at temperatures of 120, 130, 140, and 150 °C. The initial thickness of the copper films used for the oxidation measurement is 21 nm. The THz transmission through a freshly deposited 21 nm thick copper film is very low. However, as the film is heated, the THz transmission increases
3.2. THz transmission through oxidizing Cu thin films

Figure 3.2: (a) Electric field of the THz pulse transmitted through a silicon wafer with (red) and without (black) a thin copper film. The copper film thickness is 9 nm. (b) Amplitude spectra obtained after fourier transforming the electric field of the THz pulses.
with time. The rate of increase is much higher at a temperature of 150 °C than at 120 °C, even though the temperature difference is only 30 °C. For the three highest temperatures used, the transmission reached its highest, final value within 3 hours, suggesting that the oxidation is complete. For the lowest temperature, the transmission continues to increase even after this time. Apparently, at this temperature, the oxidation is incomplete even after 3 hours.

In order to study the oxidation kinetics, we need to extract the information about the instantaneous thickness of the oxide layer from the above data. Copper can oxidize to form two oxides, cuprous oxide (Cu$_2$O) or cupric oxide (CuO). However, for heating temperatures below 225 °C, it is known that the oxide formed is predominantly cuprous oxide [118]. Hence, at any particular instant of time during oxidation, the sample consists of the silicon substrate, a remaining copper layer and a cuprous oxide layer formed due to heating. A thin layer of cuprous oxide fully transmits the THz pulses, as do most dielectric, nonabsorbing layers which are much thinner than the wavelength of the light used. In our case, the oxide film is a few nanometers thick, whereas the THz wavelength is around 300 µm. For the same reason, we can also neglect the reflection losses at the Cu$_2$O-air interface. Therefore, the transmission through the oxidizing sample depends only on the thickness of the copper film. If we know which thickness of
the copper film corresponds to a particular value of the THz transmission, we can determine the instantaneous remaining copper film thickness during oxidation. It is tempting to calibrate our measurement by performing the THz transmission experiments on un-oxidized copper films of varying thickness, and to correlate this with the instantaneous transmission of the originally 21 nm thick film during oxidation. However, as we will show in the next section, this leads to erroneous results.

### 3.3 Thickness-dependent THz transmission

First, we attempt to model the transmission of a copper thin film using the transmission equation: \[ \frac{\tilde{E}_{tx}}{\tilde{E}_{ref}} = \frac{1 + n}{1 + n + Z_0 \tilde{\sigma}(\omega) d}, \] where \( \tilde{E}_{tx} \) is the amplitude of the THz electric field transmitted through the copper film, \( \tilde{E}_{ref} \) is the transmitted electric field through the uncoated half of the silicon wafer, and \( Z_0 \) is the impedance of free space (see also Fig.3.4(a)). \( d \) is the thickness of the copper film, and \( n_3 = 3.418 \) [123] is the frequency-independent refractive index of silicon at THz frequencies and \( \tilde{\sigma}(\omega) \) is the complex conductivity of the film. If we know the conductivity of the thin film, we can calculate the THz transmission as a function of thickness from Eq. 3.1. For a thin film, the conductivity is expected to be lower than that of bulk metal, due to the large number of intrinsic defects created during physical vapor deposition [124, 125]. The electron-beam evaporated films are polycrystalline, with distinct grain boundaries. Scattering from these grain boundaries considerably influences the properties of the film. This results in a lower conductivity of evaporated thin films compared to that of bulk metal. Hence, we adjusted the value of the conductivity of copper, so as to match the measured value of the THz transmission through a thick copper film of 37 nm. This gives a conductivity value of \( \sigma = 1.8 \times 10^7 \text{ Sm}^{-1} \). This should be compared to the DC bulk conductivity value of copper, \( \sigma = 5.6 \times 10^7 \text{ Sm}^{-1} \). The conductivity is assumed to be real and frequency-independent for the low THz frequencies. Since the THz transmission seems to be frequency-independent, only a single frequency was used in the calculation. The calculated THz transmission for copper films of different thickness is shown by the solid line in Fig. 3.4(b).
We also measured the THz transmission of un-oxidized copper films of various, known thicknesses ranging from 3 to 37 nm. Only half of the wafer was covered with the copper film and the other half was masked during evaporation (Fig. 3.4(a)). The THz transmission through the copper film and through the uncovered half of the silicon wafer was measured for each of these samples. The transmission was measured on the same day as the films were deposited, so as to minimize errors due to oxidation at room temperature. The THz beam path in the set-up was flushed with dry nitrogen gas to reduce absorption of THz light by water vapor molecules in the ambient atmosphere. In Fig. 3.4(b), the measured THz intensity transmitted through the copper film with respect to the transmission through an uncoated silicon wafer, is also plotted (dots). Starting from the thickest films, the transmission rapidly increases for decreasing film thickness, as expected. However, the transmission does not reach its maximum value when the film thickness reaches a value of 0 nm, but already at a thickness of about 7 nm. This contrasts with the transmitted THz power calculated using Eq. 3.1, which shows a transmission which gradually increases to 100% when the copper thickness becomes zero.
3.3. Thickness-dependent THz transmission

Figure 3.5: Scanning electron micrographs of thin copper films on silicon substrates, with thickness around the percolation threshold.

3.3.1 Percolation

The discrepancy between the measured and the calculated thickness-dependent THz transmission can be understood, if we examine the SEM images of the Cu thin films. In Fig. 3.5 the SEM images of the copper films for three different thicknesses: 5, 8, and 10 nm are shown. The images show that these ultra thin films do not form a smooth uniform layer. Formation of thin films by physical vapor deposition is characterized by the formation of nuclei and their subsequent growth. As the deposition continues, the nucleated metal islands grow until they coalesce to form a continuous macroscopic network. The transition from isolated islands to a connected network occurs at the so-called percolation threshold thickness, which is the effective thickness at which the electrons can completely percolate through the random metal network. The unexpected increase in the THz transmission for films of thickness $< 8$ nm can be explained on the basis of this non-uniform film morphology [124]. Below the percolation threshold, the electrons cannot move out of the metal islands and hence the film behaves
more like an insulator. For films having an effective thickness above the percolation threshold, the conductivity is still reduced with respect to the bulk value because of carrier scattering by the film inhomogeneities. The SEM images indicate that the percolation threshold occurs somewhere between 5 to 8 nm. This agrees with the percolation threshold determined from the experimental THz transmission data shown in Fig. 3.4(b). Similar results were reported and extensively studied by Walther et al. [122], for thin gold films.

### 3.3.2 Calibration of THz transmission

It is now clear why we cannot calibrate our oxidation measurements using the measured transmission of unoxidized copper films of varying thickness. Percolation considerably influences the conductivity of the deposited films. An unoxidized Cu film of 6 nm thickness will not have the same optical properties as an oxidizing copper film of which 6 nm remains as copper. The former is made up of mostly disconnected copper islands whereas the latter largely retains the optical properties of the originally 21 nm thick copper layer.

A better way to calibrate our measurements is to measure the conductivity of the unoxidized 21 nm thick copper film, where we assume that as the film oxidizes, the conductivity of the remaining copper doesn’t change. In that case, the changes in the THz transmission are caused by changes in the thickness of the remaining copper layer only. For a fully oxidized copper film, no significant differences in the THz transmission were observed for samples held at T=150 °C, and samples cooled down to room temperature. This suggests that thermal changes in the conductivity, which could in principle affect the calibration procedure, were negligible.

The average conductivity of the 21 nm thick copper films used for oxidation measurement later, was measured to be \((1.14 \pm 0.04) \times 10^7\) Sm\(^{-1}\). Applying Eq. 3.1 to the THz transmission measurement of oxidizing copper films (Fig. 3.3), we back-calculated the instantaneous copper thickness during oxidation. This is shown in Fig. 3.6(a), where we plot this calculated copper thickness as a function of oxidation time. The maximum value of the THz transmission is reached when the oxidation is complete, and is used as \(E_{ref}\) in this case. The THz transmission through the thicker films is considerably lower, which gives a lower signal-to-noise ratio. This explains the larger scatter of the data points in the calculated instantaneous copper thickness in the early stages of the oxidation. Using a surface profilometer,
we have measured the thickness of several copper films before and after complete oxidation. When completely oxidized, the thickness of the oxide layer is around 1.5 times that of the pure copper layer. To calculate the instantaneous cuprous oxide thickness during oxidation, we multiplied the used-up copper thickness by this experimentally determined factor 1.5, which gives us the instantaneous Cu$_2$O thickness. The growth of the cuprous oxide layer as a function of time is shown in Fig. 3.6(b). When the copper film is completely oxidized, the oxide layer does not grow further. This explains the saturation in the growth of the cuprous oxide thickness after a certain time.

3.4 Oxidation kinetics and Arrhenius equation

We can further analyze the temperature dependence of the oxidation rate. In the temperature range we used, the oxidation of copper is expected to follow a parabolic rate law: [126, 113]

\[
d_{\text{oxide}} = d_0 + k(T)t^{\frac{1}{2}},
\]

where \(d_{\text{oxide}}\) is the thickness of the oxide layer at time \(t\), and \(k(T)\) is the rate constant. \(d_0\) is the natural oxide layer on the copper film formed at room temperature before heating the sample. Eq. 3.2 is fitted to the oxide growth curves shown in Fig. 3.6(b). A natural oxide layer of \(d_0 = 1\) nm was assumed for all the films to obtain the best fit for the measurements. When oxidation is complete, the thickness of the cuprous oxide no longer increases. Hence the part of the curve where the thickness remains constant is not used in the fitting procedure. Generally, a parabolic rate law for the oxidation of copper thin films implies a diffusion-dominated oxidation process [127]. The activation energy for diffusion can be obtained from the temperature dependence of the rate constant \(k\), which follows the Arrhenius equation: [128]

\[
k(T) = k_0 e^{\frac{-E_a}{R} \frac{1}{T}}.
\]

Here \(k_0\) is a constant, \(E_a\) is the activation energy for diffusion, \(R = 8.314\) J mol$^{-1}$K$^{-1}$ is the universal gas constant and \(T\) is the heating temperature. If we plot \(ln(k)\) against \(\frac{1}{T}\), the slope of the straight line thus obtained is \(-\frac{E_a}{R}\). Hence, the value of the activation energy can be determined from the slope of the Arrhenius curve. The Arrhenius relation for rate constants obtained from fitting Eq. 3.2 to our oxidation data is plotted in Fig. 3.7. The activation energy for diffusion calculated from the slope of a straight line fit to this data is \(0.55 \pm 0.06\) eV.
Figure 3.6: (a) The instantaneous copper film thickness during oxidation as a function of time after calibration. (b) The instantaneous cuprous oxide thickness as a function of time. The used-up copper thickness is multiplied by a factor of 1.5 to obtain the thickness of the oxide layer as a function of time.
When a copper film is exposed to air, a native layer of oxide quickly forms on the surface of the metal film. For further oxidation to be possible, Cu\textsuperscript{+} ions have to be transported from the copper film to the interface between oxide and air by diffusion [129]. The activation energy for diffusion of Cu\textsuperscript{+} ions through the motion of vacant Cu\textsuperscript{+} sites in the opposite direction, is at least the bond energy of copper, 2 eV [130, 113]. However, the diffusion along a grain boundary can be much faster than the volume diffusion through defects in the material’s crystal structure [128]. Since the activation energy calculated from our measurements is much lower than 2 eV, we assume that the diffusion mechanism is mostly grain boundary diffusion. The activation energy of 0.55 ± 0.06 eV that we obtain is somewhat higher than that reported by Gao et al. [131] for Cu thin films at heating temperatures of 175-400 °C (0.37 eV) and comparable to that reported by Zhong et al. [113] for Cu thin films at temperatures of 180-260 °C (0.57 eV).

In conclusion, the oxidation of copper thin films on silicon substrates was studied using THz time domain spectroscopy in the temperature range of 120 - 150 °C. We find that the oxidation kinetics could be obtained by measuring the THz transmission through the heated copper films as a function of time. By relating the instantaneous transmission of the oxidizing copper films with the calculated transmission based on the measured conductivity of the copper, we were able to obtain the instantaneous copper layer thickness and, thus, the cuprous oxide layer thickness during the oxidation. Calibrating the measured THz transmission during the oxidation by com-

Figure 3.7: Arrhenius plot of $ln(k)$ versus $\frac{1}{T}$. The line is a linear fit to the measurement.
parison with the measured THz transmission through unoxidized copper layers of several thicknesses is not possible. We show that this is explained by the percolation transition of copper that occurs for average copper layer thicknesses around 7 nm. Such a transition is absent in layers of the same thickness which result from the oxidation of a layer with a much larger starting thickness. The oxidation follows a parabolic rate law from which the activation energy for diffusion is calculated to be $0.55 \pm 0.06$ eV. This value suggests a fast diffusion mechanism, such as diffusion of Cu atoms through the grain boundaries as the dominant diffusion mechanism.
4.1 Introduction

When a semiconductor is excited with ultrashort laser pulses with photons having sufficient energy, mobile charge carriers may be excited. On the surface of a semiconductor this can produce a current surge which emits THz radiation. This current surge is generally caused by either the acceleration of the photoexcited carriers by the surface depletion field, or by the photo-Dember effect arising from a difference in the mobilities of electrons and holes, in combination with a carrier concentration gradient [132, 36].

Laser-induced terahertz emission originating from a current surge at a metal/semiconductor interface has also been reported in the literature [133, 134]. A potential energy barrier for electrons can be formed at such an interface, known as a Schottky barrier junction. An electric field and a depletion layer devoid of mobile charge carriers are present at these junctions, as explained in the following section. When these junctions are illuminated with laser pulses, the semiconducting material absorbs the laser photons creating electron-hole pairs. These free carriers at the interface are then swept across the depletion layer due to the electric field present at the Schottky barrier and form a photocurrent normal to the interface. This transient photocurrent in the depletion layer radiates a sub-picosecond electromagnetic pulse, which contains terahertz frequencies.

Recently, emission of THz pulses has been observed from semiconducting thin films like silicon, germanium and cuprous oxide deposited on metal surfaces, when excited with femtosecond laser pulses [92, 135]. The THz emission from these thin films also results from the formation of a Schottky barrier, which creates a static electric field in the depletion region of the Schottky barrier. The THz emission from Au/Cu$_2$O junctions is especially
interesting, since these junctions have been reported in the literature to behave as ohmic junctions [136]—metal/semiconductor junctions which do not form a potential barrier at the interface—and not Schottky barrier junctions. For this reason we take a closer look in this chapter at the THz emission from Au/Cu$_2$O thin films, their preparation and characteristics, the optical response of the thin films, etc.

## 4.2 Metal-Semiconductor (Schottky) junctions

The junctions formed when a metal and a semiconductor are brought into contact can either be Schottky (rectifying) or ohmic (non-rectifying) depending on the work functions of the metal and the semiconductor. Schottky junctions find use in several electronic devices such as photodetectors, (Schottky) diodes, power rectifiers, microwave generators, etc. Here we consider a junction formed when a $p$-type semiconductor is in contact with a metal having a lower work function than that of the semiconductor. (The following discussion has been adapted from reference [137]).

Before contact, the metal and the semiconductor usually have different Fermi levels. When the materials are brought into contact, an exchange of charge carriers occurs by diffusion, until an equilibrium is reached. At this point, the semiconductor Fermi level falls/rises so as to have a constant Fermi level across the junction. The change in the Fermi level of the semiconductor is equal to the difference in the work functions of the two materials, $\phi_m - \phi_s$, where $\phi_m$ is the work function of the metal and $\phi_s$ that of the semiconductor (see Fig. 4.1). The charge flow due to diffusion creates a separation of charges and, hence, a contact potential and an internal electric field. The internal electric field formed eventually opposes the diffusion current, giving rise to a stationary situation.

Let us consider a $p$-type semiconductor with a higher work function than the metal, and the semiconductor Fermi energy lower than that of the metal. When contact is made between these two materials, the Fermi level of the semiconductor increases to the level of that of the metal. The energy band-bending for a $p$-type semiconductor at a Schottky junction are shown in Fig. 4.1.

The electric field across the junction and the depletion layer width can be found by using Poisson’s equation. The Poisson’s equation for one dimension can be written as

$$\frac{d^2V(x)}{dx^2} = -\frac{\rho(x)}{\epsilon_r \epsilon_0},$$  \hspace{1cm} (4.1)
4.2. Metal-Semiconductor (Schottky) junctions

where \( V(x) \) is the electric potential at the point \( x \) in the Schottky junction, \( \rho(x) \) is the charge density at the same point \( x \) in the junction and \( \varepsilon_r \) is the relative permittivity of the material. If we assume that the semiconductor is fully depleted, the charge density in the depletion region is equal to \( N_A \) the number of acceptors per \( \text{cm}^3 \). Hence the charge density in the depletion region of the semiconductor \( (0 < x < x_n) \) can be written as

\[
\rho(x) = \rho_0 = |e|N_A. \tag{4.2}
\]

Poisson’s equation for the potential in the junction region is thus

\[
\frac{d^2V(x)}{dx^2} = \frac{|e|N_A}{\varepsilon_r\varepsilon_0}. \tag{4.3}
\]

The first integral of this equation will yield the electric field as a function of position in the junction:

\[
E(x) = -\frac{dV(x)}{d(x)} = \frac{|e|N_A}{\varepsilon_r\varepsilon_0}(x - x_n), \quad 0 < x < x_n \tag{4.4}
\]

where \( x_n \) is the linear extent of ionized acceptor atom concentration in the semiconductor as measured from the interface, and is called the depletion

---

**Figure 4.1:** Energy levels at a junction between metal and p-type semiconductor, plotted as a function of position \( x \); \( E_{CB}, E_{VB} \): conduction and valence band energy levels of the semiconductor; \( E_{FS}, E_{FM} \): Fermi energy levels of the semiconductor and metal respectively; \( \phi_s, \phi_m \): Work functions of the semiconductor and metal respectively, \( V_c \): Schottky barrier contact potential.
Chapter 4. THz emission from Cuprous oxide thin films

Figure 4.2: (a) Charge density $\rho$ versus position $x$ in a junction formed by a metal and p-type semiconductor, after equilibrium is reached. $x_m$ and $x_n$ are the extends of charge density into the metal and the semiconductor respectively and $qN_A$ is the charge density present at the depletion layer. (b) Electric field $E$ as a function of the position. At the interface the strength of the electric field ($E_{max}$) is maximum at the junction and extends to a depth $x_n$ in the semiconductor.

width. It can be seen from this equation that the electric field is maximum at the interface and decreases to zero across the depletion region, as shown in Fig. 4.2(b).

The second integral of Poisson’s equation can yield the electric potential or contact potential,

$$V_c = \frac{|e|N_A x_n^2}{2\varepsilon_r \varepsilon_0}$$  \hspace{1cm} (4.5)

The depletion width can be solved from the above equation to yield,

$$x_n = \sqrt{\frac{2\varepsilon_r \varepsilon_0 V_c}{|e| N_A}}$$  \hspace{1cm} (4.6)

The charge density distribution of a Schottky junction is shown schematically in Fig. 4.2(a). The metal has a surface charge density due to the holes at the metal surface that originate from the semiconductor. The extent of this charge density into the metal is determined by the mean free path of the charge carriers, which depends on the metal. Since a real metal has some resistivity due to electron-phonon collisions, there is a small electric field inside the metal. The p-type semiconductor has a charge density extending into the semiconductor due to the ionized acceptors as also shown in Fig. 4.2(b). There is a greater penetration of the junction electric field
4.3 Cuprous oxide as a semiconductor

Cuprous oxide (Cu₂O) is one of the two stable phases of oxides of copper, the other one being cupric oxide (CuO). Cuprous oxide is reddish in colour with a direct band gap of 2 eV, whereas cupric oxide has a dark gray colour with a band gap of 1.4 eV [138]. Cuprous oxide crystallizes in a cubic structure as shown in the Fig. 4.3 [139]. The copper atoms form face-centered cubic lattices (fcc) and the oxygen atoms form body-centered cubic lattices (bcc). Some of the properties of Cu₂O are given in Table. 4.1.

From a historical point of view, it is interesting to note that cuprous oxide is the oldest material in semiconductor electronics [142]. Before the discovery of silicon, germanium, and other semiconductors, Cu₂O was recognized as a potential semiconductor for the fabrication of solar cells. The advantages offered by Cu₂O are that

- It is a non-toxic material
- The starting material, Cu, is very abundant
- The production process is simple
Table 4.1: Properties of cuprous oxide. [138, 140, 141]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band gap</td>
<td>2.0 eV</td>
</tr>
<tr>
<td>Electron affinity</td>
<td>3.2 eV</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>Simple cubic</td>
</tr>
<tr>
<td>Lattice constant</td>
<td>4.27 Å</td>
</tr>
<tr>
<td>Melting point</td>
<td>1235 °C</td>
</tr>
<tr>
<td>Density</td>
<td>6.0 g cm$^{-3}$</td>
</tr>
<tr>
<td>Conductivity type</td>
<td>p type</td>
</tr>
<tr>
<td>Lowest TO phonon resonance</td>
<td>4.4 THz</td>
</tr>
</tbody>
</table>

The semiconducting properties of Cu$_2$O are mainly the result of the imperfections in its crystal structure. In some solids, the stoichiometry could be violated, as the ratio of atoms in them is slightly different from the ideal ratio. Such non-stoichiometric compounds balance their structures by the presence of defects [143]. Sears and Fortin [140] reported that an excess of oxygen is the major active impurity in Cu$_2$O and gives a p-doped semiconductor. There are also reports that Cu$_2$O is intrinsically copper deficient due to the formation of copper vacancies that act as a source of holes [144]. The presence of impurities like Si, N etc. can also impart p-type semiconducting properties to cuprous oxide [145, 146].

The first device based on the semiconducting properties of cuprous oxide, was a back-wall copper oxide rectifier, fabricated by L. O. Grondahl in 1920 [147]. Preliminary results on forming a photocell by the reduction of a cuprous oxide surface to form a Cu/Cu$_2$O Schottky barrier was also reported by him [148]. Schottky barrier junction solar cells are the most studied of Cu$_2$O based solar cells. The most serious concern regarding Cu$_2$O based solar cells has been the poor efficiency caused by the reduction of cuprous oxide to copper near the metal interface [136]. Due to this phenomenon, most metals like Al, Cu, Cr, Mg etc. form a Schottky barrier height of 0.7 - 1.0 eV, which in fact is the barrier height associated with a Cu/Cu$_2$O interface. All metals were found to be capable of reducing Cu$_2$O at the interface, except gold, silver and thallium. Gold and silver have been reported to form, essentially, ohmic contacts.
4.4 THz generation from Au/Cu$_2$O thin films

4.4.1 Sample preparation

Gold substrates are prepared by electron beam evaporation of Au onto a clean silicon wafer in vacuum. A thin film of chromium is also evaporated onto the silicon substrate prior to the deposition of gold, in order to improve the adhesion of gold to the silicon substrate. The chromium and gold layers are each 50 nm thick. A thin film of copper is then evaporated onto the gold substrate. The Cu thin film is then completely oxidized by thermal oxidation in ambient air at a temperature of 220 °C, to get Cu$_2$O thin films. The thickness of the Cu$_2$O thin film formed after oxidation is about 1.5 times that of the original copper thin film. Although copper can form at least two types of stable oxides, it has been observed that for temperatures lower than 250 °C, Cu$_2$O is predominantly formed [118, 102].

4.4.2 Experimental set-up and results

The experimental set-up used for our THz generation measurements is schematically shown in Fig. 4.4. We use 50 fs laser pulses from a Ti:Sapphire laser centered at a wavelength of 800 nm. The average power of the laser source is 2.5 W and the repetition rate is 5.2 MHz. The laser beam is split
into pump and probe beams by a 90:10 beam splitter. 90% of the laser power is used for the generation of THz pulses from the Au/Cu$_2$O thin films. The samples are mounted in a reflection-type configuration, and the laser is incident on the sample at an angle of 45°. The pump pulses are delayed using a retro-reflecting mirror arrangement mounted on a translation stage. The generated THz pulses are collected, collimated and focussed onto a 300 $\mu$m GaP crystal which acts as an electro-optic detection crystal [33]. The probe beam is also focussed onto the detection crystal through an aperture in the last parabolic mirror. The electric field of the THz pulse modifies the polarization state of the 800 nm probe beam which is measured using an arrangement of a quarter wave plate, a Wollaston prism, and a differential detector. The setup was purged with dry nitrogen gas in order to reduce the absorption by water vapor in the atmosphere. The spectrum of the measured THz pulse is obtained by Fourier transforming the time-dependent THz electric field.

The electric field as a function of time of the single-cycle THz pulse emitted from $\sim$420 nm thick Cu$_2$O on gold and the corresponding Fourier-transformed amplitude spectrum are shown in Fig. 4.5. The bandwidth of the emitted THz pulse ranges from 0.1 to $\sim$7 THz. The dip seen around 4.46 THz in the emission spectrum, is a transverse-optic (TO) phonon resonance of Cu$_2$O, indicating that the sample is polycrystalline in nature and not amorphous, which is also confirmed by x-ray diffraction measurements. In the THz frequency range, Cu$_2$O has two TO phonon resonances, at 4.4 and 18.3 THz [141, 149]. The asymmetric shape of the THz emission spectrum around the 4.46 THz resonance observed in our measurement is due to the strong refractive index modulation in this region caused by the phonon resonance, which can be explained as follows. The variation of the real and imaginary part of the refractive index of cuprous oxide around the phonon resonance has been studied by Dawson et al. [141] and is shown in Fig. 4.6. It can be seen that around the phonon resonance there is a strong asymmetry in the real part of the refractive index of cuprous oxide. Since the reflection/transmission at the Cu$_2$O/air interface depends on the frequency-dependent refractive index of Cu$_2$O, we can see the asymmetry of the refractive index also reflected in the generation spectrum. Around 4.5 THz a peak is seen in the recorded THz emission spectrum, which is due to the fact that the real part of refractive index is $\sim$1 at this frequency. Thus at 4.5 THz, the radiation does not experience a reflection loss at the Cu$_2$O/air interface. This is seen as a peak at the same frequency in the recorded THz emission spectrum.
4.4. THz generation from Au/Cu$_2$O thin films

Figure 4.5: (a) Electric field of the THz pulses emitted from a 420 nm thick cuprous oxide film on gold substrate, and (b) the corresponding fourier transformed spectrum.

Figure 4.6: Frequency-dependent real ($n$) and imaginary ($k$) parts of the complex refractive index $\tilde{n} = n + ik$ of Cu$_2$O around the phonon resonance at $\sim 4.4$ THz [141].
4.5 Interface between gold and thermally formed Cu$_2$O

The most plausible explanation for THz generation from Au/Cu$_2$O junctions is carrier acceleration by the Schottky barrier electric field near the Au/Cu$_2$O interface. However, earlier reports indicate that the junctions formed when Au is deposited on Cu$_2$O, are essentially ohmic in nature [136]. In order to verify the formation of a Schottky junction when Cu$_2$O thin films are fabricated on gold substrates, we measured the current voltage (I-V) characteristics of one of the samples. The measured I-V characteristic of such a sample is shown by the solid red line in Fig. 4.7. We can see that the junction formed by the oxidation of a Cu film deposited on Au has a non-linear I-V curve. We also made a sample where, first, the Cu was deposited and oxidized to Cu$_2$O, followed by the deposition of Au. The junction formed by this sample is characterized by a linear I-V curve (dashed line in Fig. 4.7), typical of an ohmic junction. This interesting result can be explained as follows. The barrier height of a Schottky interface depends on the work function of the metal. The samples used for terahertz emission experiments are thermally formed Cu$_2$O thin films on gold substrates. During the process of heating copper to get the oxide film, inter-metallic compounds, or alloys, of Au/Cu can be formed by diffusion [150]. In our experiments, this would mean that the interface we have is not an Au-Cu$_2$O interface, but an AuCu-Cu$_2$O interface. Since Cu and Cu$_2$O can form a Schottky junction, it is likely that a AuCu/Cu$_2$O actually does give rise to a Schottky-like junction. Note that although the non-linearity of the I-V curve is indicative of a barrier formation, a deviation from the ideal behavior of a Schottky diode is observed. The nearly point symmetric nature of the observed I-V curve is currently under investigation.

In order to investigate the presence of the AuCu diffusion layer, we removed the thermal oxide film from the gold substrate by treating it with dilute nitric acid. A color contrast enhanced photograph of a pure gold substrate and a gold substrate after removing the Cu$_2$O film is shown in Fig. 4.8. The surface of the gold substrate, obtained after removal of the oxide layer, has a rose-gold color, clearly indicating the presence of an interfacial diffusion layer [151]. To confirm this, X-ray analysis of these substrates was also performed.

X-ray diffraction patterns were recorded in a Bragg-Brentano geometry in a Bruker D5005 diffractometer equipped with a Huber incident-beam monochromator and Braun PSD detector. Data collection was carried out
4.5. Interface between gold and thermally formed Cu$_2$O

Figure 4.7: Measured current-voltage (I-V) characteristics of the Au/Cu$_2$O junctions. The solid line shows the non-ohmic junction characteristics of a Cu$_2$O thin film fabricated on a Au thin film substrate and the dashed line shows the ohmic junction characteristics when the Au thin film is deposited on the Cu$_2$O thin film. For the case of Cu$_2$O formed on Au, it is now known that the Au and Cu form a AuCu alloy.

Figure 4.8: A photograph of the AuCu alloyed sample surface. The right side of the sample was alloyed, and looks brownish. The left side of the sample is a pure gold surface. The image was processed to obtain a better color contrast.
Figure 4.9: XRD measurement of the gold substrates from which the oxide was removed. No trace of oxide was found in the substrate.

at room temperature using Cu Kα1 radiation as the source. Evaluation of the measured data was done with the Bruker program EVA. All patterns are background-subtracted, meaning that the contribution of air scatter and possible x-ray fluorescence radiation, is subtracted.\footnote{We are grateful to Ruud W. A. Hendrikx, Department of Materials Science and Engineering, TU Delft, for the X-ray measurements.}

The XRD pattern obtained from the cleaned gold substrate with the rose-gold surface is shown in Fig. 4.9 in black. The colored sticks correspond to the peak positions and intensities of the Au and AuCu alloy, taken from the ICDD pdf4 database \[152\]. The intensity vs. 2θ values from the ICDD database correspond to the diffraction pattern from powdered samples with no preferential crystal orientation. It is possible to confirm the presence of a material if the position of the measured diffraction peaks in the 2θ axis matches with the position of the peaks in the database (the colored sticks). We see that in our measurement, the measured diffraction peak positions coincide with the peak positions of a Au-Cu alloy, in addition to gold and the silicon substrate. The electron-beam evaporated thin metal films usually have a preferred crystallographic orientation and, hence, the relative size of the intensities of the diffraction peaks doesn’t correspond to that of the powdered sample given in the database. The measured x-ray diffraction peak at a 2θ value of 39° suggests the presence of both Au and AuCu in the sample, but around angles 45°, 79°, and 83°, the measured
peaks coincide better with the expected peak positions of the AuCu alloy. This proves that inter-diffusion compounds of Au and Cu are formed at the interface. From the peaks around 38° and 82°, it can be argued that some Au is also present in its pure form. From the XRD analysis, the alloy is estimated to have a composition of Au$_{0.8}$Cu$_{0.2}$. However, since nitric acid can dissolve Cu, we note that the process of removing the Cu$_2$O layer could have caused some changes in the actual composition of the alloy layer. It can also be argued that the composition of the alloy may also vary in depth and laterally due to inhomogeneities in the diffusion. However, we do not see a proof for this from the XRD analysis, since the presence of several compositions would have given rise to more peaks in the XRD measurement. The main intention here is to show the presence of an inter-diffusion layer, and its importance in the THz generation process from our samples.

4.6 Variable-Angle Spectroscopic Ellipsometry

Spectroscopic ellipsometry allows for accurate measurements of the optical properties of thin films. In this technique, the change in polarization state of the light reflected from the thin film-substrate system is measured and is expressed by two values ($\Psi$, $\Delta$) which are defined by the ellipsometric equation [153]

\[ e^{i\Delta} \tan(\Psi) = \rho = \frac{r_p}{r_s}. \]  

Here $r_p$ and $r_s$ are the complex Fresnel reflection coefficients of the sample for p- and s-polarized incident light. $\Psi$ and $\Delta$ represent the angles determined from the amplitude ratio and phase difference between the reflected p- and s-polarized components. A model is constructed to calculate the values of ($\Psi$, $\Delta$) using various parameters such as optical constants, layer thicknesses, surface roughness, etc. The generated and the experimentally determined values of $\Psi$ and $\Delta$ are compared and one or more model parameters are adjusted to fit the experimental data. This is done in an iterative manner until a good fit is reached between the measured and the experimental spectra. In variable-angle spectroscopic ellipsometry, these values are measured over a wide range of wavelengths and angles of incidence, which helps to minimize errors in extracting the material properties.

We performed ellipsometric measurements using a Variable Angle Spectroscopic Ellipsometer (VASE, J.A.WoollamCo.) in the wavelength region from 600 nm to 1600 nm and at different angles of incidence varying from 45° to 60°. Initially, we fabricated individual thin films of Au and Cu$_2$O
Figure 4.10: $\Psi$ and $\Delta$ measurements of the light reflected from a cuprous oxide thin film on gold substrate. Both $\Psi$ and $\Delta$ are plotted in units of degrees.

on silicon wafers, and measured the $(\Psi, \Delta)$ values of the light reflected from these samples. The refractive indices were obtained from the best fit model. The gold film was modelled to have a Drude-like conductivity. The frequency-dependent refractive indices of the gold film were measured because the properties of a thin film deposited by e-beam evaporation may be different from that of the bulk, since they depend on the conditions of evaporation like the chamber pressure, rate of deposition, etc.

We then measured the $(\Psi, \Delta)$ values of the light reflected from a thin Cu$_2$O film on Au, formed by the thermal oxidation of copper. Based on the
assumption that there is an inter-diffusion layer of AuCu formed at the interface, we included this layer in the model. Hence, the model consists of the AuCu alloy film on gold (which was considered as the substrate), and the Cu$_2$O layer with surface roughness. At the start of the fitting procedure, the thickness of the pure gold film and the AuCu alloy was set to 50 nm and 0 nm, respectively, and was then allowed to vary during the iterations. The refractive index of AuCu was allowed to vary in the model, and the frequency-dependent refractive indices of the material were parametrized by means of B-splines, which provide a numerical tool for data fitting, without considering any physical model [154]. A B-spline consists of an array of control or ‘knot’ points and a set of interpolating polynomial functions. The permittivity values of the material assumed by the model at the knot points are so as to generate ($\Psi$, $\Delta$) values which match with the experimentally measured ones. The imaginary part of the frequency-dependent dielectric permittivity of the material is modeled as the B-spline function and the real part is calculated from the Kramers-Kronig relations. The imaginary part of the refractive index, $k$ is forced to be always positive, to make physical sense. Measured optical constants of the evaporated 50 nm Au film were used as the starting values for fitting that of the AuCu film. The frequency-dependent refractive indices of the Cu$_2$O thin film were also parametrized by means of B-splines. For Cu$_2$O, the initial values of the refractive index were taken from the measured values for a different oxide film on a silicon substrate.

The values of $\Psi$ and $\Delta$ for the sample from the experiment and the best
fit model are shown in Fig. 4.10. The colored solid lines correspond to the measured $\Psi$ and $\Delta$ at different angles of incidence and the dashed black lines show the values calculated using the model. A good fit is obtained between the measurement and the model, as can be seen from the figure. The optical constants of the Au-Cu alloy and Cu$_2$O from the best-fit model are given in Fig. 4.11. The thickness of the Cu$_2$O thin film was around 232 nm with a roughness of 23 nm. This agrees well with the average roughness ($\sim 21$ nm) measured using the AFM (see Fig. 4.12). Increasing the thickness did not have any effect on the model generated values of $(\Psi, \Delta)$, indicating that the thickness of the AuCu film is larger than the penetration depth. The penetration depth of light of wavelength 700 nm in the AuCu thin film was calculated to be around 8 nm.

### 4.7 Thickness dependence of pump power absorption and THz emission

As mentioned earlier, the band gap of Cu$_2$O is $\sim 2$ eV. The wavelength of the pump laser used for the THz emission experiments, is centered around 800 nm, which corresponds to an energy of 1.5 eV. At this wavelength, the absorption coefficient $\alpha$ of bulk Cu$_2$O has a small value of $9.42 \times 10^3$ cm$^{-1}$ [155]. In our THz generation model, charge carriers are generated in the Cu$_2$O film by absorbing the laser photons, which then accelerate in the Schottky electric field to result in THz emission. The small absorption
4.7. Thickness dependence of pump power absorption and THz emission

Figure 4.13: (a) Transmission and reflection of pump laser pulses (50 fs, 800 nm) through Cu$_2$O thin films on glass, as a function of the oxide thickness and (b) the pump power absorption extracted from the data in (a).

The coefficient of Cu$_2$O is surprising, considering the strong THz emission from Au/Cu$_2$O thin films. In order to investigate the absorption of 50 fs, 800 nm laser pulses by thin films of cuprous oxide, several thin film samples were made of varying thickness on glass substrates. As before, the oxide films were prepared by heating thin films of copper at a temperature of $\sim$220 °C in the ambient atmosphere. The thickness of the original copper films was varied from 40 nm to 300 nm, in steps of 20 nm. The absorption of 800 nm laser pulses was measured by recording the power transmitted and reflected from the oxide film and then subtracting it from the incident power.

Fig. 4.13(a) shows the measured reflected and transmitted laser power as a function of the Cu$_2$O thickness, normalized to the incident power. There is an oscillatory behavior in the pump power reflectance and transmittance as a function of the oxide thickness. This is due to the Fabry-Perot-like oscillations inside the oxide film, occurring due to the reflections at both the oxide-air interface and the oxide-glass interface. The power absorbed by the Cu$_2$O thin films is shown in Fig. 4.13 (b). The absorption generally increases, but superimposed on this increase are the oscillations due to the Fabry-Perot etalon effect. The maximum absorption among the films measured is $\sim$ 26% for an oxide thickness of 360 nm.

The THz emission from Cu$_2$O films on Au substrates also depends on the thickness of the oxide layer [135] as shown in Fig. 4.14. The electric field of the THz radiation emitted from Cu$_2$O/Au samples is plotted as a function
Chapter 4. THz emission from Cuprous oxide thin films

Figure 4.14: Amplitude of THz electric field emitted from Cu$_2$O/Au samples as a function of the oxide thickness (black). In blue is the corresponding pump power absorption. (adapted from Ref. [135])

of the oxide thickness (dots). The squares correspond to the pump power absorption in these samples. A much stronger absorption of the pump laser pulses is seen in the case of Cu$_2$O films deposited on Au. For example, for a Cu$_2$O thickness of 65 nm on Au, the absorption is already 55%. This should be compared with the 6% absorption observed for the same Cu$_2$O thickness on glass. The absorption increases as a function of thickness and also shows etalon effects. The maximum pump power absorption seen is almost 75% for a Cu$_2$O film thickness of 420 nm. The THz emission also increases with the pump power absorption, but faster. The maximum THz emission occurs for oxide thicknesses at which the reflection is minimized due to the etalon effect. For the right thicknesses, multiple reflections occur at the Au/Cu$_2$O and Cu$_2$O/air boundaries, which increases the optical path length of the laser pulses inside Cu$_2$O. This enhances the laser-light absorption inside the material. This is also called the cavity-resonance effect.

4.8 Multilayer reflection: Calculation and experiment

As mentioned in the previous section, the THz emission from a Cu$_2$O/Au interface is proportional to the amount of laser power absorbed in the oxide film. At an optimum thickness, the Cu$_2$O film can act as its own antireflection coating and, hence, increase the absorption inside the sample at
4.8. Multilayer reflection: Calculation and experiment

(a) (b)

Figure 4.15: (a) Measured and (b) calculated reflection spectra of Cu$_2$O layers of different thicknesses on a gold substrate, normalized to the reflection from a bare gold substrate.

a particular wavelength. Knowing the reflection spectra of the Cu$_2$O thin films on oxide substrates we can find the thickness at which the reflection minimum occurs at the pump laser wavelength, 800 nm. Since we have extracted the frequency-dependent refractive indices of the Cu$_2$O and AuCu thin films, we can calculate the reflection spectra of the oxide films on the AuCu substrate for various thicknesses. We also experimentally measured the broadband reflection spectra of samples of five different Cu$_2$O thicknesses on AuCu substrates, to validate the complex refractive indices of the materials obtained from the ellipsometer analysis (refer Section 4.6).

To measure the reflection spectrum, a Tungsten halogen lamp (HL 2000, Ocean optics) was used as the broadband visible light source. The light from the source was passed through a polarizer and was incident upon the samples at 45° angle of incidence. The spectrum of the reflected light was measured using an Ocean Optics spectrometer. The Cu$_2$O layer thicknesses of the samples used in the experiment were measured using the variable angle spectroscopic ellipsometer. The intensity of the light reflected from the oxide film on the gold substrate was measured as a function of wavelength and normalized to the reflection from a bare gold film. The reflectivity spectra thus obtained for five different Cu$_2$O film thicknesses are plotted in Fig. 4.15(a). The calculation of the wavelength dependent reflectivity, also normalized to the reflection from a bare gold film, was done with an analytical solution [156] which is suitable for multilayers containing strong absorbing elements such as metals. The calculated reflection spectra are shown in Fig. 4.15 (b). The multilayer stack considered for the reflection coefficient calculation consists of the silicon substrate, a 50 nm thick Cr
film, 50 nm AuCu layer and the Cu$_2$O film. To calculate the reflection spectra, we used the frequency-dependent complex refractive-index of the materials which was obtained from analyzing the ellipsometry measurements. We can see that there is a good agreement between the calculated and the measured reflection spectra. The dashed blue curve in Fig. 4.15(b) shows the reflection spectrum of a sample with a 223 nm thick Cu$_2$O film, calculated without considering the formation of AuCu layer, but considering pure gold as the substrate. It can be seen that this does not match well with the experimentally measured spectrum for the same oxide thickness. In particular, the position of the calculated minimum at $\sim$855 nm is off compared to the measured one at $\sim$820 nm. The thickness of the oxide layer of this sample was also measured independently using a surface profilometre to be $\sim$ 225 nm, which is very close to the value of 223 nm extracted from the ellipsometer measurement. The minimum in the calculated reflection spectrum of this sample occurs at a different wavelength in the case of AuCu alloy instead of Au as the substrate for the Cu$_2$O layer, since the dielectric function of AuCu is different compared to Au. Hence there is a difference in the phase change on reflection compared to that from Au, leading to the shift in the calculated minimum in the reflection shown in Fig. 4.15(b). A good agreement between the measured and calculated reflection spectra was obtained only when the AuCu thin film was considered in the calculation, again supporting the presence of the inter-diffusion AuCu alloy layer and validating the optical constants derived from the ellipsometer measurements. The small discrepancies between the calculated and measured reflection spectra could be due to a combination of several issues. The reflection calculation, for example, ignores the roughness of the oxide film in the calculation, the lateral inhomogeneities in the refractive index of the Cu$_2$O layer, and experimental errors in determining the angle of incidence. It can also be seen from the calculated and reflected spectra that an oxide film of $\sim$225 nm thickness is well suited for THz emission applications, since it has a very low reflection coefficient at 800 nm, which is the pump laser wavelength used in THz generation experiments.

4.9 Application: Tapered waveguide

One of the main applications of optoelectronic THz transmitters and receivers is terahertz absorption spectroscopy for the characterization of molecules and crystals. Often, there is a need to identify very small quantities of a material. A promising solution appears to be the use of THz
waveguides for frequency-dependent absorption measurements using THz time-domain spectroscopy [157]. THz spectroscopy using metal parallel-plate waveguides (PPWG) has also been demonstrated by Melinger et al. [158]. They used the transverse electromagnetic (TEM) mode of the metal PPWG to probe the properties of a thin polycrystalline film dropcast onto one of the metal plates. The advantage of performing spectroscopy using a PPWG is that only micrograms of a sample are required due to the spatial confinement. In addition, high spatial resolution THz absorption spectra measurements are possible due to the 2D spatial confinement [159]. It was reported that PPWG terahertz time domain spectroscopy can be sensitive even to nanometer-thick water layers on surfaces [160]. THz waveguides have also been used for the characterization of Bragg and non-Bragg stop bands of metal slits [161], photonic crystals [162], terahertz band gap properties [161, 163], etc.

However, an important issue limiting the use of THz-waveguides is reflection losses due to the inefficient coupling between the guided and freely propagating THz waves. An increase in the measurement sensitivity is obtained by decreasing the plate separation of the PPWG, but this comes at the cost of reducing the energy coupled into the waveguide. To increase the coupling of THz radiation to these narrow waveguides, silicon lenses are used. However, the refractive index of silicon is high and this results in the loss of THz radiation by reflection from the silicon lenses. The reflection losses at the silicon lenses essentially suppress the advantage of using a
waveguide for high sensitivity measurements. Recently, it was shown that the use of a tapered parallel plate waveguide can improve THz coupling to the narrow gap of the waveguide [164, 165]. In the conventional quasi-optic approach (shown in Fig. 4.16 (a) [top figure]), most of the THz light is reflected by the silicon surfaces. By tapering the metal surface of the parallel plate waveguide, the changes in the waveguide gap are introduced gradually [166]. In other words, the width of the PPWG changes slowly with respect to the wavelength and hence the reflection losses can be minimized.

Utilizing the THz emission properties of Cu$_2$O on metal substrates, we put forward a new method for achieving efficient coupling into the parallel plate waveguide. The tapered PPWG can be modified in such a way that instead of coupling THz radiation into the PPWG, we can generate the THz radiation inside the waveguide itself. In this approach, one of the metal plates is a copper plate having a thin film of cuprous oxide on its surface. An aluminium plate is used on the other side in the parallel plate configuration. The pump laser illuminates the copper plate with the oxide surface at a grazing angle, as shown in Fig. 4.16(a) [bottom figure]. The experimental setup is the same as Fig. 4.4. A 500 $\mu$m ZnTe crystal is used for THz detection. A photograph of the waveguide is shown in Fig. 4.16(b). The THz signal generated and guided out from the waveguide is shown in Fig. 4.17(a). The Fourier-transformed spectrum of the THz signal is shown in Fig. 4.17(b). The spectrum consists of components from 0.5 THz to almost 4 THz. Apart from the spectroscopic applications, this kind of waveguide can also be used to concentrate THz radiation in subwavelength-
sized focal spots. The spot size of the THz beam at the end of the waveguide is determined by the plate separation at the out-coupling end. By reducing this in the x- and y-directions, it is possible to achieve sub-wavelength THz spot sizes. This can also have important applications in sub-wavelength imaging using THz frequencies.
5.1 Introduction

In the previous chapter we saw that Au/Cu$_2$O Schottky junctions can emit broadband THz radiation when excited with femtosecond laser pulses. It was observed that the bandwidth of the THz generation extends up to almost 8 THz. The THz light generated from Au/Cu$_2$O thin films with an optimized Cu$_2$O film thickness is almost half as powerful as the emission from a 300 µm GaP crystal, which is another THz source capable of such broadband THz emission. Understanding the THz emission mechanism of these emitters could help us to further increase the emitted THz power, perhaps leading to a broadband and strong THz source. The possible THz emission mechanisms include: optical rectification occurring due to Schottky electric-field-induced second-order nonlinearities [167] in Cu$_2$O, acceleration of photoexcited charge carriers in the Schottky field, or internal photoemission of holes over the Schottky barrier [168]. In any case, the formation of a Schottky junction seems to be critical for the THz emission. In this respect it is logical to propose that localizing the pump light at the interface — where the Schottky electric field is the maximum — can result in an increase in the efficiency of these THz emitters. One way to achieve this is by exciting so-called surface plasmons at the metal/Cu$_2$O interface.

It has been shown that the strong local electromagnetic fields associated with surface plasmons can give rise to stronger optical absorption [59] and stronger fluorescence [169], and can enhance nonlinear processes like second-harmonic generation [65], Raman scattering [170] etc. Recent attention has also focused on the use of surface plasmons to enhance the emission from known THz emitters in several ways. It has been demonstrated that surface plasmons, excited using random, as well as ordered nanostructures, can enhance the terahertz emission from thin gold films [85, 69, 70]. Emission of
terahertz radiation is also observed when surface plasmons are excited on a thin unstructured film of gold deposited on a glass prism and excited in the so-called Kretschmann geometry [71]. Most recently, plasmonic photoconductive antennas have been shown to enhance the terahertz emission compared to conventional photoconductive antennas [72, 73]. Interleaved plasmonic electrodes were used with the photoconductive antenna by Berry and Jarrahi [73], where the interleaved electrodes were used to reduce the transit time of the generated carriers to the electrodes. It was illustrated, through simulations, that the plasmonic nature of the interleaved electrodes increases the pump power absorption inside the photo-conducting material. However, the relation between the THz emission and the plasmonic nature of the electrodes was not experimentally demonstrated.

In this chapter, we demonstrate that Au/Cu$_2$O Schottky interfaces capable of emitting terahertz radiation can be nano-structured to support surface plasmon modes, and that this leads to enhanced THz generation. The nanostructures we have shown are Cu$_2$O covered gold gratings of various periodicities. We argue that the efficiency of the THz generation is improved because surface plasmon excitation leads to increased optical absorption near the interfaces where the Schottky electric field is the strongest. Coupling of light into plasmons at the laser excitation wavelength is confirmed using white-light reflection spectroscopy. The THz emission, as well as the pump power absorption, show a dependence on both the azimuthal angle of the sample when rotated around the surface normal, and on the periodicity of the grating, clearly highlighting the role played by the grating in enhancing the THz emission. It is shown that the plasmon mode is essential in enhancing the THz emission.

5.2 The concept of a plasmon-enhanced Schottky emitter

A schematic diagram showcasing the idea of a nano-structured metal/semiconductor thin film THz emitter is shown in Fig. 5.1. A gold nano grating is fabricated and covered with a thin Cu$_2$O film. Femtosecond laser pulses centered around a wavelength of 800 nm are used to pump a Au/Cu$_2$O thin film THz emitter at an angle of incidence of 45°, and surface plasmons are optically excited at the interface. The optical field of the pump laser is thus localized near the interface between Au and the oxide thin film. The objective behind the work described in this chapter is
5.2. The concept of a plasmon-enhanced Schottky emitter

Figure 5.1: Nanostructured Au/Cu$_2$O Schottky-junction THz emitter. The pump laser pulses are incident on the sample, generating THz pulses. A nano-grating is fabricated at the interface to excite surface plasmons and hence enhance the THz generation.

to exploit this localization of the pump laser electric field near the metal surface to increase the THz emission from the Au/Cu$_2$O thin films.

Fig. 5.2 shows the schematic of the coordinate system used to describe the orientation of the grating, angle of incidence of the pump laser beam, etc. The polar angle $\theta$ is the angle of incidence, that is the angle between the incident laser beam and the normal to the sample surface. The azimuthal angle $\phi$ is the angle between the plane of incidence of the laser beam and the grating vector. The polarization of the incident laser beam is defined with respect to the plane of incidence. When the electric field vector of the incident light is parallel to the plane of incidence, we call it TM or p-polarized radiation. If the electric vector of the incident light is perpendicular to the plane of incidence, it is called TE or s-polarized radiation.

5.2.1 Plasmon excitation at the Au/Cu$_2$O interface

The nano-grating at the interface between the Au and Cu$_2$O thin film adds or subtracts positive integer multiples of the grating wavevector to the in-plane wavevector of the incident laser light. If the total in-plane wavevector matches with the surface plasmon wavevector of the same frequency, the incident light excites surface plasmons. The phase-matching condition to be satisfied in order to couple surface plasmons to the interface when $\phi =$
Incident beam

Figure 5.2: The coordinate system used in this chapter for describing the orientation of the grating and the incident beam: The polar angle $\theta$ is the angle of incidence of the laser beam as measured from the surface normal. The azimuthal angle $\phi$ is the angle between the plane of incidence of the pump laser and the grating vector. $\Lambda$ is the periodicity of the grating.

$0^\circ$ (see Fig. 5.2) is given by\(^1\):

$$k_{inc,x} \pm Nk_g = k_{sp}, \quad N = 1, 2, 3, \ldots \quad (5.1)$$

where $k_{inc,x}$ is the real component of the incident wavevector, parallel to the interface in the x-direction and $k_{sp}$ is the wave vector of the surface plasmon. $k_g = \frac{2\pi}{\Lambda}$ is the grating wavevector, $N$ is an integer and $\Lambda$ is the periodicity of the grating. Assuming that the relative permittivity of the dielectric $\epsilon_d$ is real and that the metal has a complex relative permittivity $\epsilon_m = \epsilon'_m + i\epsilon''_m$, with $\epsilon''_m < |\epsilon'_m|$, the real part of the surface plasmon wave vector can be expressed as

$$k'_{sp} = \frac{2\pi}{\lambda} \sqrt{\frac{\epsilon_d\epsilon'_m}{\epsilon_d + \epsilon'_m}}, \quad (5.2)$$

where $\lambda$ is the vacuum wavelength of the incident light. The x-component of the incident wave vector is $k_{inc,x} = \frac{2\pi n}{\lambda} \sin \theta$, $n = \sqrt{\epsilon_d}$ is the refractive index of the dielectric, and $\theta$ is the angle at which light is incident on the grating (Fig. 5.2).

\(^1\)The plasmon coupling condition [74] for non-zero azimuthal angles is described in section. 2.2.1
In reality, the permittivity of the dielectric $\epsilon_d$ can also be complex, but this does not change the physical picture very much. For an angle of incidence of 45° on the Cu$_2$O thin film, the required periodicity of a grating which can couple surface plasmons to a gold-cuprous oxide interface can be calculated from Eq. 5.1 to be $\sim 240$ nm. The full complex, electric relative permittivity values of Cu$_2$O and Au are $\epsilon_d = 5.39 + i0.28$ [135] and $\epsilon_m = -26.15 + i1.85$ [171], at a free space wavelength of 800 nm, the wavelength of the pump laser used.

### 5.3 Sample fabrication and characterization

The basic steps involved in the fabrication of nano-structured Au/Cu$_2$O thin film THz emitters are outlined in Fig. 5.3. To fabricate the nano-grating, we use electron beam lithography (EBL) and reactive ion etching (RIE). The first step in fabricating the nano-grating is to spin-coat an e-beam sensitive resist onto cleaned silicon wafers. We used ZEP 520A (a product of ‘Zeon Chemicals’) as the e-beam sensitive resist which is a 1:1 copolymer of $\alpha$-chloromethacrylate and $\alpha$-methylstyrene. It is a highly sensitive, stable and durable positive-tone resist [172]. The high sensitivity of ZEP in comparison with PMMA —Poly (methyl methaacrylate) —is advantageous as it reduces the electron-beam exposure time for fabricating large area structures. An adhesion promotion layer of hexamethyldisilazane (HMDS) was applied to the silicon substrate prior to spin-coating the ZEP e-beam resist. The grating pattern was written onto the resist layer using an electron beam pattern generator. The exposure to an e-beam causes chemical changes in the resist layer, influencing the solubility of the exposed area in comparison with the unexposed area. For positive resists such as ZEP, the exposed area becomes more soluble in the developing agent compared to the unexposed area. After the e-beam exposure, the samples were developed by treating them in N-amyl acetate for 90 s and in a 1:9 solution of IPA$^2$ : MIBK$^3$ for 30 s. After development, the samples were dried using the flow from a nitrogen gun. The grating pattern was then etched into the silicon substrate by using a reactive ion etching system, using SF$_6$ gas as the etchant. An etch rate of around 1.3 nm/s was observed for silicon. It is to be noted that this etch rate was recorded at a bias voltage of $\sim 260$ V and that it depends on the applied RF power. The resist layer which remains after etching Si was then removed using an oxygen plasma etch.

---

$^2$Isopropyl alcohol

$^3$Methylisobutylketone
Figure 5.3: Schematic representation of the basic steps in the sample fabrication process. (a) Spin coating of the resist on Si substrate (b) Electron-beam exposure and development (c) dry etching (d) Oxygen plasma cleaning (e) Cr and Au evaporation (f) Cu evaporation and oxidation to form Cu$_2$O film (Drawing not to scale).

After transferring the grating pattern onto the silicon wafer by dry etching, thin films of chromium and gold were deposited onto the grating surface. These metal films were deposited by electron beam evaporation in a vacuum chamber, at a pressure of around $10^{-6}$ mbar. The chromium layer is required to improve the adhesion of gold to the silicon substrate. The thin films of gold and chromium both have a thickness of 50 nm. A cuprous oxide layer on the gold grating was fabricated by first depositing a copper thin film by e-beam evaporation and by subsequently oxidizing it in the ambient atmosphere at a temperature of 250$^\circ$ C.

The surface characterization of the fabricated nano-gratings were done using a scanning electron microscope (SEM) and an atomic force microscope (AFM). Fig. 5.4 (a) shows an AFM image of one of the fabricated nanogratings after etching the silicon. AFM imaging is necessary to measure the etch-depth of the grating. The grating structure is retained after the deposition of metal thin films Cr and Au, as can be seen from the SEM image of the gold grating surface (see Fig. 5.4 (b)). The surface of the deposited Cu film also follows the grating profile. However after oxidation to form Cu$_2$O, the surface of the oxide layer shows only vaguely the grating profile, as can be seen from the SEM and AFM images of the oxide surface over the gold grating shown in Fig. 5.5 (a) and (b) respectively. By removing the oxide layer from one of the samples and then examining it under the SEM, we also confirmed that the oxidation process of the Cu did not affect the shape of the gold nano-grating.
Figure 5.4: (a) An AFM image of a fabricated nano-grating after etching Si. (b) The SEM image of the grating after the deposition of Au. The periodicity of the grating shown is 240 nm, with an etch depth of 40 nm.
5.4 Experimental Setup

The setup used for THz emission experiments is shown in Fig. 5.6. Briefly, we use 50 fs laser pulses with a centre wavelength of 800 nm from a Ti:Sapphire oscillator (Scientific XL, Femtolasers, Vienna) with an average power of 800 mW and a repetition rate of 11 MHz. The laser beam is split into a pump beam and a probe beam by a 90:10 beam splitter. The high power pump beam is incident on the fabricated sample at an angle of 45° and the THz emission was recorded in the reflection configuration. The pump pulses are delayed using a retro-reflecting mirror arrangement mounted on a loudspeaker oscillating at 50 Hz. The generated THz pulses are collected, collimated and focused onto a 500 μm (110) ZnTe crystal which acts as an electro-optic detection crystal. The probe beam is also focused onto the detection crystal through a hole in the last parabolic mirror. In the electro-optic crystal, the instantaneous electric field of the THz pulse elliptically polarizes the probe beam. The ellipticity induced in the probe beam is measured using a system of a quarter-wave plate, a Wollaston prism, and a differential detector, and is proportional to the instantaneous THz electric field. By varying the delay between the THz and probe pulses we can measure the full THz electric field as a function of time in a stroboscopic manner.
5.5 Plasmon-enhanced THz emission

The measured THz emission from a nano-structured Au/Cu$_2$O film with a grating periodicity of 240 nm, an etch depth of $\sim$40 nm and a Cu$_2$O thickness of $\sim$166 nm is shown in Fig. 5.7(a). The sample is excited with p-polarized pump pulses. On the x-axis is the time in ps and on y-axis is the electric field of the emitted THz pulse in arbitrary units. In black is the electric field of the pulse emitted from a patterned Au/Cu$_2$O interface, at an azimuthal angle of 0°, which is the azimuthal angle at which we expect that surface plasmons are excited.

The THz pulse emitted by a flat (non-structured) Au/Cu$_2$O interface is also shown in Fig. 5.7(a) for comparison (blue line). Compared to the THz emission from the flat samples, nano-structuring the interface increases the strength of the emitted THz electric field by a factor of $\sim$5.6. In order to verify that the grating is indeed the reason for the observed THz emission enhancement, we measured the THz emission after rotating the grating to an azimuthal angle of 90°, at which no plasmons are excited. The THz...
Figure 5.7: (a) Time-dependent p-polarized electric field of the THz pulses emitted by the flat and the nano-structured Au-Cu$_2$O thin film interfaces, after optical excitation with p-polarized pump pulses with a wavelength of 800 nm. The THz pulses emitted when the azimuthal angles are 0° and 90° are shown for the nano-structured sample. An enhanced THz emission is seen from the nano-structured sample, when the grating grooves are perpendicular to the polarization of the incident pump laser pulses. The periodicity and etch depth of the grating are 240 nm and 40 nm respectively. The thickness of the cuprous oxide film is \( \sim 166 \) nm. (b) Illustration of the azimuthal angle \( \phi \) in the experimental configuration. The sample surface lies in the xy-plane, and xz is the plane of incidence of the pump beam. To change the azimuthal angle, the grating is rotated about the z-axis.
emission from the nano-structured sample at this orientation is shown in red in the Fig. 5.7(a). The THz emission is only weakly enhanced for this grating orientation. It can be seen that the orientation of the grating has a significant effect on the THz emission from the nano-structured thin films. This substantiates the role played by the grating in enhancing the THz emission from Au/Cu$_2$O thin film samples. In order to achieve the desired azimuthal angle, the grating is rotated about an axis perpendicular to the sample surface, while the plane of incidence of the laser beam remains the same. This is illustrated in Fig. 5.7 (b).

The dependence of the THz emission on the orientation of the grating can be interpreted as an indication of the excitation of surface plasmons at the Au/Cu$_2$O interface. In order to excite surface plasmons, a component of the electric field of the incident light perpendicular to the metal surface is necessary. For p-polarized laser light incident on the sample at $\phi = 0^\circ$, this condition is satisfied and, hence, surface plasmons can be excited. However, for s-polarized light, there is no component of the incident light perpendicular to the metal surface at $\phi = 0^\circ$ and hence no plasmon excitation is possible. We experimentally observe that an enhancement of the THz emission occurs only when the configuration is favorable for plasmon excitation.

The enhancement of the THz emission from the grating samples also shows a dependence on the etch depth of the grating. The THz emission from the nano-structured thin films was measured for three different grating etch depths —23 nm, 33 nm, and 55 nm. Figure 5.8 shows the time dependent electric field of the THz pulses emitted from these three samples, compared to the THz emission from a non-structured sample. The Cu$_2$O film thickness deposited on these nano-gratings was around 166 nm. The sample with an etch depth $d \sim 55$ nm shows the maximum THz emission enhancement. In this case, the emitted THz electric field is larger than the emission from the flat sample by a factor of around 5.8. Note that this corresponds to a power enhancement factor of $\sim 33$. The samples with a lower etch depth also showed an enhanced emission, with electric field enhancement factors of around 2.9 and 4.0, for etch depth values of 23 nm and 33 nm respectively.

In order to better understand the role of surface plasmons in the enhanced THz generation, we measured the azimuthal-angle dependence of the pump laser absorption as well as the THz emission from these three grating samples. Fig. 5.9 compares the variation of the electric-field amplitude of the emitted THz light with respect to the increase in the pump power absorp-
Figure 5.8: (a) Electric field of the THz pulses emitted by the flat and the nano-structured Au-Cu$_2$O thin film interfaces with varying etch depths of the grating. The grating etch depths of the samples shown are 23 nm (black line), 33 nm (red line), and 55 nm (blue line). The THz pulse emitted by the non-structured sample (green) is also shown for comparison.

Absorption resulting from surface plasmon excitation, for $\phi$ varying from $-90^\circ$ to $90^\circ$. The black points show the percentage of the incident light which is absorbed inside the nano-structured Au/Cu$_2$O thin film samples. In all the three samples ($d = 23$, 33, and 55 nm), the maximum absorption is seen when $\phi = 0^\circ$. The blue points show the electric field amplitude of the THz pulses emitted from these samples. To make a comparison between the emission from the three samples, the emission is normalized to the THz emission from the sample with an etch depth of 54 nm, at $\phi = 0^\circ$. It can be seen that the maximum THz emission from each of the samples also occurs at $\phi = 0^\circ$.

When the azimuthal angle is varied from $\pm 90^\circ$ to $0^\circ$, the increase in THz emission strength is faster than the increase in the pump power absorption. For example, for an etch depth of 33 nm, as we vary the azimuthal angle $\phi$ from $-90^\circ$ to $0^\circ$, the optical absorption increases by a factor of about 1.8, but the peak-to-peak electric field of the THz emission increases by a factor of 3.2. This faster increase in the THz emission is an indication of the important role of plasmons in enhancing the THz emission. When plasmons are excited, the electric field of the pump laser is concentrated at the Au/Cu$_2$O interface. This increases the absorption and charge car-
5.6 Reflection spectroscopy measurements

Linear white light spectroscopy is an important tool in plasmonics, and is used to characterize the plasmon resonances. To understand the physical origin of the spectral response of the nanograting samples, we measured the reflection spectra from a few samples with varying periodicity. Nanogratings of periodicities varying from 220 nm to 300 nm were made on gold and then covered with Cu$_2$O. While fabricating the gratings, the width of the grooves of the different gratings was kept constant at 140 nm, and only the width of the ridge was varied to achieve different periodicity (see

Figure 5.9: Azimuthal angle dependence of the pump power absorption and the THz emission from the nano-structured Au/Cu$_2$O thin films, for three different grating etch depths. The absorption of the pump laser pulses (p-polarized) is expressed as a percentage of the incident laser power and is shown in black. The blue squares show the measured peak-to-peak electric field of the emitted THz pulses, after normalizing to the emission from the sample of etch depth 54 nm, at an azimuthal angle of 0°. The lines are guides to the eye.
While changing the periodicities of the gratings, only the width of the ridges was varied and the width of the grooves was kept constant at 140 nm.

Fig. 5.10. This was done to avoid a periodicity dependence for any resonance which depends on the groove width, and hence, propagating surface plasmons would be the only periodicity dependent feature in the reflection spectra.

To measure the reflection spectrum of the grating samples we used a tungsten halogen light source and an ‘Ocean Optics’ spectrometer. The measurements were made for the spectral range from 600 nm to 1000 nm. The experimental setup used for the reflection spectra measurements is shown in Fig. 5.11. The light from the output of the light source is collimated using a lens of focal length 5 cm, and then passed through a polarizer mounted on a rotation stage. The polarized light is then focussed by another lens of focal length 10 cm onto the nano-structured Au/Cu$_2$O sample at a 45 degree angle of incidence. The light reflected by the sample is collimated and focused onto a fiber-optic receiver by a pair of lenses of focal length 10 cm and 5 cm respectively. The optical fiber sends the collected light to a spectrometer and the spectrum is then analyzed with a computer.

To normalize the reflection spectra from the nano-structured Au/Cu$_2$O thin films, we first obtain a reference spectrum by measuring the reflection from a bare gold surface. The reference spectrum thus obtained is shown in Fig. 5.12. The reflection spectra measured from the nano-structured samples $R_{\text{GRATING}}(\Lambda)$ were divided by the reference measurement $R_{\text{GOLD}}(\Lambda)$ (see Fig. 5.11 (b)). Hence the quantity plotted in the reflection spectroscopy analysis of the nano-structured samples shown in this chapter can be de-
5.6. Reflection spectroscopy measurements

Figure 5.11: (a) A schematic of the experimental setup for reflection spectroscopy. The spectrum of the light reflected by the sample is measured using a spectrometer. (b) The reflection spectrum of a bare gold surface is used to normalize the spectral response of the nano-structured Au/Cu$_2$O films. $R_{\text{GRATING}}$ is the reflection from the nano-structured Au/Cu$_2$O films and $R_{\text{GOLD}}$ is that from a bare gold surface. L$_1$ and L$_2$ lenses used to focus the light onto the sample and L$_3$, and L$_4$ collect the reflected light to the spectrometer.

Figure 5.12: The spectrum of the light reflected by a bare gold surface. This is used as a reference for normalizing the reflection spectra of Au/Cu$_2$O thin films.
fined as

\[ R(\lambda) = \frac{R_{\text{GRATING}}(\lambda)}{R_{\text{GOLD}}(\lambda)}. \] \hspace{1cm} (5.3)

### 5.6.1 p-polarized incident light

First we measured the reflection spectra of the nano-structured Au/Cu$_2$O samples of varying periodicity when the incident light is p-polarized and the azimuthal angle \( \phi = 0^\circ \). The Cu$_2$O film thickness on all the samples is around 166 nm. In Fig. 5.13, we plot the reflection spectra of the nano-structured Au/Cu$_2$O thin films, normalized to the reflection spectrum of a bare gold surface. The inset shows the orientation of the grating and the laser polarization with respect to the plane of incidence. The reflection spectra were measured for gratings with periodicities varying from 220 to 300 nm. In all the reflection spectra, a dip is seen around a wavelength of 660 nm. This occurs due to the destructive interference caused by the multiple reflections at the oxide boundaries [173, 92], as explained in the previous chapter. This etalon dip in the reflection spectra is independent of the grating periodicity as it only depends on the average thickness of the Cu$_2$O film over the Au substrate.

In Fig. 5.13, another resonance is observed which does depend on the grating periodicity, which is suggestive of a plasmonic character. This plasmon resonance is seen around a wavelength of 980 nm for a sample with grating periodicity of 300 nm. The plasmon resonance shifts to lower wavelengths when the periodicity is reduced. For a periodicity of 230 nm, the plasmon resonance is around a wavelength of 800 nm, corresponding to the excitation laser wavelength. The spectrum of the incident laser beam is indicated by the red graph close to the x-axis, around a wavelength of 800 nm. The plasmon resonances are quite broad, which could be attributed to the high absorption coefficient in the surrounding medium, which increases the plasmon bandwidth [174].

To confirm the plasmonic nature of the resonances we observe in the reflection spectra, we also measured the reflection spectra of these samples for the case when the azimuthal angle of the grating is 90°. The spectra measured in this configuration are shown in Fig. 5.14. As mentioned before, the plasmon resonances depend on the orientation of the grating with respect to the incident laser polarization. Here, since the grating grooves are now parallel to the incident laser polarization, we do not observe any dips in the reflection spectra in the 800 - 1000 nm wavelength range.
5.6. Reflection spectroscopy measurements

![Graph](image)

**Figure 5.13:** White light reflection spectra of the nano-structured Au/Cu$_2$O thin films, when $\phi = 0^\circ$. The different colored lines correspond to the different periodicities of the nano-grating. The periodicity is varied from 220 nm to 300 nm. The thickness of the Cu$_2$O film is around 166 nm. The incident light is p-polarized. This configuration is suitable for plasmon excitation. The inset on the lower right shows the orientation of the grating, and the polarization of the incident laser pulses during the measurement. Also shown (in red) is the spectrum of the pump laser pulses used in the THz generation experiment.

In the samples used in all the measurements till now, the interference minima, corresponding to absorption maxima, do not coincide with the laser excitation wavelength, which is around 800 nm. This was done to move the interference minimum to a different wavelength than the plasmon dip but only for the purpose of proving that clear plasmon excitation occurs. However, the optimum thickness of Cu$_2$O for a good emitter is when the reflection minimum coincides with the excitation laser wavelength, maximizing the pump laser absorption. Hence we also prepared a set of nano-structured samples with a Cu$_2$O film of approximately 232 nm thickness. The reflection spectra from these samples were measured and normalized by dividing them with the bare gold reflection spectrum, and are shown in Fig. 5.15. It can be seen that the interference minima occur at a wavelength of $\sim$ 840 nm, which is closer to the pump laser wavelength of 800 nm. In Fig. 5.15, the dip in the reflection spectra caused by the interference is marked by the red arrows. For a grating of periodicity 300 nm, the plasmon resonance is clearly visible around a wavelength of 1000 nm. For gratings
of periodicities close to 230 nm, the plasmon resonance merges with the reflection minimum near to the laser excitation wavelength. As a guide to the eye, the approximate plasmon resonance positions are marked with black arrows. Another set of plasmon resonances can also be seen in Fig. 5.15, in the spectral range 600 - 750 nm. For the grating of periodicity 300 nm, this plasmon resonance occurs at a wavelength near to 750 nm, and shifts to lower wavelengths as the periodicity is decreased. These plasmon modes correspond to the case $N = +1$, where $N$ is the grating diffraction order.

The wavelengths at which the plasmon resonances are expected for the various grating periodicities can be calculated from the dispersion relation given by Eq. 5.1. The frequency-dependent complex refractive indices of the AuCu alloy and the Cu$_2$O thin films, extracted from ellipsometer measurements, were used to calculate the resonance wavelengths. In Fig. 5.16, we plot the wavelengths of the plasmon resonances which occur in a nano-structured Au/Cu$_2$O sample, as a function of the grating periodicity $\Lambda$. In the wavelength range we consider, two plasmon resonances are possible, corresponding to $N = \pm 1$. The plasmon modes calculated from Eq. 5.1 corresponding to $N = -1$, as a function of the grating periodicity are shown.
5.6. Reflection spectroscopy measurements

Figure 5.15: White-light reflection spectra of the nano-structured Au/Cu$_2$O thin films, for a 232 nm thick Cu$_2$O thin film. The grating periodicities vary from 220 nm to 300 nm as before and $\phi = 0^\circ$. The incident light is p-polarized. The interference minima in the spectra are marked with the red arrows, and the plasmon resonances, corresponding to $N = -1$, are marked by the black arrows. For a periodicity of 230 nm, the plasmon resonance merges with the thin film interference minimum.
as the solid black line and the ones corresponding to \( N = +1 \) are shown as the dashed black line. The peak plasmon wavelengths observed experimentally through the reflection spectroscopy measurements are also plotted in the same figure. The scattered points in red show the plasmon resonance wavelengths measured from the set of samples with an oxide film thickness of 232 nm, and in blue are the measured resonances from the samples with an oxide film of thickness 166 nm. The plasmon resonance wavelengths corresponding to \( N = +1 \) are not shown for the samples with a \( \text{Cu}_2\text{O} \) thickness of 166 nm, since these plasmon resonances occur near to the interference minimum around 650 nm, and were impossible to determine. The plasmon resonance wavelengths observed experimentally are close to the expected values. The differences between the measurements and calculations may be attributed to the error in the extracted refractive index values of the AuCu alloy and the \( \text{Cu}_2\text{O} \) thin film. It can also be seen from Fig. 5.16 that the wavelengths at which plasmon resonances are experimentally observed match better with the analytically calculated resonance wavelengths for a \( \text{Cu}_2\text{O} \) thickness of 232 nm, compared to a thickness of 166 nm. This could be due to the fact that for the analytical calculation, the thickness of the \( \text{Cu}_2\text{O} \) layer is considered infinite. In other words, we ignore the effects of having a finite \( \text{Cu}_2\text{O} \) layer while determining the expected resonance wavelength for a particular grating periodicity. Perhaps in this case, the extent of the plasmon field in the z-direction is such that it “feels” the presence of the air and thus experiences a different refractive index.

### 5.6.2 s-polarized incident light

To couple electromagnetic incident waves to surface plasmons, an electric field component perpendicular to the interface is required to set up the necessary surface charges. Hence, while using grating coupling at an azimuthal angle \( \phi = 0^\circ \), we require p-polarized incident light for the excitation of the surface plasmons. However, when \( \phi = 90^\circ \), it is possible to excite surface plasmons using s-polarized incident light. In the case of a grating, the surface of the metal has been “folded”, which allows both s and p-polarized incident light to have a component of the electric field vector normal to the metal surface, depending on the orientation of the grating grooves with respect to the plane of incidence. When the azimuthal angle \( \phi = 90^\circ \), s-polarized incident light has the electric field vector normal to the slope of the ridges of the grating and can excite surface plasmon polaritons, as shown in Fig. 5.17 [175, 176].
5.6. Reflection spectroscopy measurements

Figure 5.16: The wavelengths at which surface plasmon resonances occur at Au/Cu$_2$O interfaces are plotted as a function of the grating periodicity. The dashed and the solid lines correspond to the expected plasmon resonance wavelengths from an analytic calculation, corresponding to $N = +1$ and $N = -1$ respectively. In the calculation, only a Au/Cu$_2$O interface is considered, and the finite thickness of the films is not taken into consideration. The blue triangles represent the experimentally determined resonance wavelengths for samples with a 166 nm thick Cu$_2$O layer on them. The red circles and squares represent the experimentally determined resonance wavelengths for samples with a 232 nm thick Cu$_2$O layer on them, and correspond to the $N = +1$ and $N = -1$ cases respectively. For the sample of oxide thickness 232 nm, the plasmon resonance and the etalon minimum wavelengths coincide near to a sample periodicity of 230 nm. The error bars are to indicate the uncertainty in determining the exact wavelengths of the plasmon resonances, from the reflection spectra measurements.
Chapter 5. Plasmon-enhanced THz emission from Schottky junctions

Figure 5.17: (a) At an azimuthal angle $\phi = 0^\circ$, s-polarized incident light has no electric field component perpendicular to the grating surface (field polarization is represented by the black arrows, running parallel to the grating lines), but (b) at $\phi = 90^\circ$, s-polarized light has an electric field component perpendicular to the metal surface. For illustration purposes, we have shown the plane of incidence of the pump laser to have rotated by $90^\circ$ in (b), but in the actual experiment, the sample is rotated instead of the pump laser beam.

Hence, we also measured the spectra of the light reflected from nano structured Au/Cu$_2$O thin films for s-polarized incident light, and for the two cases when $\phi = 0^\circ$ and $\phi = 90^\circ$. In Fig. 5.18 (a) we plot the spectra of the light reflected from the nano structured Au/Cu$_2$O thin films at $\phi = 0^\circ$, for s-polarized incident light, and normalized to the intensity reflected by a bare gold surface. The reflection spectra correspond to different grating periodicities ranging from 220 nm to 300 nm, as before. In Fig. 5.18(b) we plot the reflection spectra of the same set of samples at $\phi = 90^\circ$, with the incident light s-polarized. It can be observed that when the incident light is s-polarized, dips in the reflection spectra corresponding to surface plasmons are observed only for the case when $\phi = 90^\circ$ (Fig. 5.18 (b)). The plasmon resonances are quite broad, and the resonance peak coincides with the excitation laser wavelength for a grating periodicity around $\sim 260$ nm. The sharp resonances seen in the reflection spectra when $\phi = 0^\circ$ (Fig. 5.18 (a)), do not correspond to plasmon dips calculated analytically. These resonances are probably due to the excitation of grating coupled waveguide modes inside the Cu$_2$O layer [177].
5.6. Reflection spectroscopy measurements

Figure 5.18: White light reflection spectra of the nano-structured Au/Cu$_2$O thin films, for *s*-polarized incident light at (a) $\phi = 0^\circ$ and (b) $\phi = 90^\circ$. The measurements correspond to different grating periodicities varying from 220 nm to 300 nm and a Cu$_2$O thickness of 166 nm.
5.7 THz emission as a function of the grating periodicity

In order to provide more evidence that the plasmon resonances we observe in the reflection spectroscopy are correlated with the enhancement of THz emission from the nano-structured samples, we also measured the THz emission from the set of samples with varying grating periodicities. In Fig. 5.19(a) we plot the electric field of the THz pulses emitted by the nano structured Au/Cu$_2$O samples, as a function of the grating periodicity. The Cu$_2$O thin film thickness is around 166 nm. In Fig. 5.19(b) we plot the THz emission from the set of samples with a Cu$_2$O thickness of around 232 nm. The azimuthal angle $\phi$ is 0° in both measurements. In both graphs, the black squares represent the peak-to-peak electric field of the THz pulses emitted by the nano-structured interfaces for p-polarized incident light. Each of these samples also has a part where the Au/Cu$_2$O interface is not nano-structured. The THz emission from these flat Au/Cu$_2$O interfaces for p-polarized incident light are shown in Fig. 5.19(a) and (b) as red dots. Similarly, the THz light emitted by the nano-structured and the flat samples for s-polarized incident light is represented by the blue and green triangles respectively. From Fig. 5.19(a) and (b), the following observations can be made:

1. For the two Cu$_2$O thicknesses, 166 nm and 232 nm, when the incident light is p-polarized and $\phi = 0^\circ$, the THz emission from the nano-structured samples (black squares) is enhanced compared to the emission from the flat samples (red dots), and the maximum enhancement occurs near to a grating periodicity of 230 nm.

2. When the incident light is s-polarized (and $\phi$ remaining $0^\circ$), we do not observe an enhancement in the emitted THz pulse amplitude (blue line), compared to the emission from the flat samples (green line).

3. In all samples, THz emission from plain Au/Cu$_2$O samples using s-polarized incident light is lower than when using p-polarized incident light.

As both graphs have different arbitrary units along the vertical axes, the amplitudes between them may differ and should not be compared. However, experimentally it was observed that the THz emission from a sample with periodicity 230 nm and Cu$_2$O thickness 232 nm was about 1.4 times higher
5.7. THz emission as a function of the grating periodicity

Figure 5.19: Peak-to-peak values of the electric field of the THz pulses emitted from flat and nanostructured Au/Cu$_2$O thin films for a Cu$_2$O thickness of (a) 166 nm and (b) 232 nm. The y-axis values of the two graphs (a) and (b) are plotted in different arbitrary units and hence the values cannot be compared. The azimuthal angle is 0° in both cases. The THz emission measured from the flat samples for p and s-polarized incident pump laser pulses are shown as red dots and green triangles respectively. The black squares represent the THz emission from the nano-structured samples for p-polarized pump laser pulses and the blue triangles show the same for s-polarized incident laser pulses. The maximum THz enhancement is seen around a periodicity of 230 nm, for both sets of samples (Cu$_2$O thickness 166 nm and 232 nm), with p-polarized incident light. The lines are guides to the eye.
than that from a sample of the same periodicity and thickness 166 nm. Surface plasmon excitation occurs, as verified using the reflection spectroscopy measurements, only for p-polarized incident pump light in the case of $\phi = 0^\circ$. The maximum enhancement in the emitted electric field of the THz pulses occurs when the grating periodicity is near to 230 nm, which is also roughly the periodicity for which we observe the plasmon resonance at the laser excitation wavelength in the reflection spectra measurements. This makes it very likely that the plasmon resonance we observe in the reflection spectroscopy measurements is responsible for the enhanced THz emission from the nano-structured samples. Assuming that the plasmons are involved in enhancing the THz emission, it is expected and observed that the THz amplitude emitted by the nano-structured samples for s-polarized pump laser is not enhanced compared to the emission from the flat samples. This is because surface plasmons cannot be excited at the Au/Cu$_2$O interface in this configuration.

The strength of the THz emission from flat Au/Cu$_2$O samples using s-polarized incident light is lower than when using p-polarized incident light, presumably because s-polarized light has a higher reflection coefficient at the air/dielectric interface than p-polarized light. Hence, for s-polarized light, less power is coupled into the Cu$_2$O thin film, resulting in lower THz emission. In principle, the THz emission from all the flat samples with the same thickness of Cu$_2$O thin film, should be of equal strength. However, the small changes in the strength from these samples for the same incident light polarization, probably occur due to the slight variations in refractive index, thickness, etc. arising from unintentional variations in the fabrication procedure.

The THz emission measured for the grating samples at an azimuthal angle of $\phi = 90^\circ$ is shown in Fig. 5.20 for p- and s-polarized incident light, for (a) 166 nm and (b) 232 nm thick Cu$_2$O layer on the metal grating. As expected, the s-polarized incident light gives rise to enhanced THz emission compared to the emission from a flat sample. From the reflection spectroscopy measurements for samples covered with 166 nm of Cu$_2$O, the grating periodicity required for plasmon coupling at an azimuthal angle of $90^\circ$ is around 260 nm, with s-polarized incident light (Fig. 5.18(b)). This is close to the grating periodicity of 250 nm, where the maximum emission is observed in Fig. 5.20(a). Similarly, when s-polarized pump light is used, enhanced THz emission is seen from the nano-structured Au/Cu$_2$O samples of oxide thickness 232 nm (Fig. 5.20(b)). The corresponding white-light reflection spectra of these samples are shown in Fig. 5.21. The approximate plasmon resonance wavelengths are marked by the arrows and appear
5.7. THz emission as a function of the grating periodicity

Figure 5.20: Peak-to-peak values of the electric field of the THz pulses emitted from flat and nanostructured Au/Cu$_2$O thin films for a Cu$_2$O thickness of (a) 166 nm and (b) 232 nm. The azimuthal angle is 90°. The THz emission measured from the flat samples for p- and s-polarized incident pump laser pulses are shown as red dots and green triangles respectively. The black squares represents the THz emission from the nano-structured samples for p-polarized pump laser pulses and the blue triangles shows the same for s-polarized incident laser pulses.

slightly shifted compared to those from samples of oxide thickness of 166 nm. However, it can be seen that the plasmon resonance is closer to the laser excitation wavelength for a sample of periodicity 280 nm, which also shows the strongest THz emission, compared to the other samples for s-polarized incident laser light.
Figure 5.21: White-light reflection spectra of nano-structured Au/Cu$_2$O samples of varying periodicities and oxide thickness 232 nm, for \textit{s}-polarized incident light and $\phi = 90^\circ$. The approximate plasmon resonance wavelengths are marked by the arrows.
5.8 Azimuthal angle dependence

5.8.1 Enhanced THz emission: significance of exciting plasmon modes

To understand the importance of plasmon excitation in enhancing the THz emission, we measured the variation of the pump power absorption and the THz emission of a few nano-structured Au/Cu$_2$O samples as a function of the azimuthal angle. These measurements are similar to those in Fig. 5.9, but here, the Cu$_2$O layer is 232 nm thick. In Fig. 5.22, we plot this for the nano-structured Au/Cu$_2$O thin films with (a) $\Lambda = 280$ nm and (b) $\Lambda = 230$ nm. The thickness of the Cu$_2$O layer on both samples was around 232 nm. Note that at this thickness, there is a maximum at a wavelength of 800 nm in the thickness-dependent pump-power absorption due to the etalon effect. The percentage of the incident pump power absorbed by the samples is represented by the black points in both graphs. The blue points show the peak-to-peak values of the electric field of the emitted THz pulses. The THz electric field amplitude is normalized to that emitted by the sample with $\Lambda = 230$ nm, at $\phi = 0^\circ$. In the first case ($\Lambda = 280$ nm), the grating periodicity does not support the excitation of surface plasmons at the Au/Cu$_2$O interface (at the incident laser wavelength), whereas in the second case the grating periodicity, $\Lambda = 230$ nm, is suitable for plasmon excitation. Stronger enhancement of the THz emission occurs when the periodicity is suitable for plasmon excitation. For this sample, when the azimuthal angle is varied from -90$^\circ$ to 0$^\circ$, the percentage of absorbed pump power increases from about 75\% to 90\%. However, for the same change in the azimuthal angle, the electric field strength of the emitted THz pulses increases by a factor of $\sim3$ (shown as the blue line), which is a much more dramatic increase compared to the increase in the absorbed pump power.

A peculiar feature is that the pump power absorption of the sample with $\Lambda = 280$ nm (Fig. 5.22(a)) shows a peak at $\phi = \sim45^\circ$. Surprisingly, this peak in the laser absorption is accompanied by a reduction in the emitted THz amplitude. We also see similar behaviour for the samples with a Cu$_2$O film thickness of $\sim166$ nm and $\Lambda = 280$ nm, which is shown in Fig 5.23(a). The peak in the absorption and the corresponding decrease in the THz emission are also observed but this time at an azimuthal angle of around 30$^\circ$. These peaks in the absorption are also observed in the visible light reflection spectra of these samples, as discussed in the next section.
Figure 5.22: The percentage of the pump power absorbed by (black) and the electric field amplitude of the THz pulses emitted (blue) from the nanostructured Au/Cu$_2$O thin films, as a function of the azimuthal angle $\phi$. (a) $\Lambda = 280$ nm, corresponding to the case of no plasmon excitation, and (b) $\Lambda = 230$ nm, corresponding to the plasmon excitation case. The thickness of the Cu$_2$O thin film is $\sim 232$ nm, and the incident light is p-polarized.

Figure 5.23: The percentage of the pump power absorbed by (black), and the electric field amplitude of the THz pulses emitted from (blue) the nanostructured Au/Cu$_2$O thin films, as a function of the azimuthal angle $\phi$: (a) grating periodicity $\Lambda = 280$ nm corresponding to the case of no plasmon excitation, and (b) $\Lambda = 230$ nm corresponding to the plasmon excitation case. The thickness of the Cu$_2$O thin film is $\sim 166$ nm and the incident light is p-polarized.
5.8.2 Reflection spectra vs azimuthal angle

To understand the nature of the plasmon resonances further, we also measured the visible light reflection spectra as a function of the azimuthal angle. Fig. 5.24(a) and (b) show the measured reflection spectra of the nanostructured Au/Cu$_2$O thin films with $\Lambda = 280$ nm, for oxide thicknesses around 166 nm and 232 nm respectively. The incident light is p-polarized in all the cases. The color bar indicates the reflected intensity, normalized to the reflection from a bare Au surface. The normalized reflected intensity is plotted as a function of the wavelength along the x-axis and as a function of the azimuthal angle $\phi$ along the y-axis. The minimum in the reflection spectrum occurring due to the multiple reflections at the interfaces of the Cu$_2$O thin film is seen at a wavelength of $\sim 650$ nm in Fig. 5.24(a) and is marked as ‘E’. The oxide thickness of this sample is $\sim 166$ nm. The plasmon resonance is at a wavelength of $\sim 925$ nm at $\phi = 0^\circ$ and is marked as -1 in the figure. When $\phi$ is changed from 0 to 90$^\circ$, the plasmon resonance disappears, since the polarization of the pump laser pulses becomes parallel to the grating grooves at $\phi = 90^\circ$. Fig. 5.24(b) shows the reflection spectra of the sample with $d_{\text{oxide}} = \sim 232$ nm, in which the etalon dip occurs a little above our wavelength of interest, 800 nm. In this case, two resonances due to plasmon excitation are visible at $\phi = 0^\circ$, at wavelengths $\sim 730$ nm and 975 nm respectively, corresponding to the $N = +1$ and -1 diffracted orders. These are marked as +1 and -1.

We also simulated the reflection spectra using an in-house developed program called ‘Cyclops’, based on the finite element method. Refractive indices of the Cu$_2$O and AuCu thin films used were obtained from the ellipsometer measurements described in chapter 4. In order to have a better match with the experimental plasmon resonance wavelength, the real part of the frequency-dependent refractive index of the Cu$_2$O film was decreased by 7%. The thickness of the oxide was then adjusted accordingly so that the etalon resonance wavelength does not change. The simulated reflection spectra of the samples with oxide thicknesses 171 nm (corresponding to 166 nm with earlier refractive indices) and 250 nm (232 nm earlier) and a grating periodicity of 280 nm are shown in Fig. 5.24 (c) and (d) respectively. The simulated spectra show a good match with the measured spectra. It was observed from the calculations that the strength of the plasmon resonances depends critically on the etch depth of the grating. The etch depth was assumed to be 17 nm in the simulations, which provided a better match with the experimentally measured reflection spectra. However, the measured etch depth is around 50 nm, and this discrepancy is assumed to
Figure 5.24: The experimental and simulated reflection spectra of nanostructured Au/Cu$_2$O thin films of periodicity 280 nm, normalized to the reflection from a bare gold surface and plotted as a function of the azimuthal angle. (a) measured, $d_{\text{oxide}} \approx 166$ nm, (b) measured, $d_{\text{oxide}} \approx 232$ nm (c) simulated, $d_{\text{oxide}} = 171$ nm (d) simulated, $d_{\text{oxide}} = 250$ nm. The colormap of the simulations in figure (d) is slightly changed from the other three in order to highlight the diagonal feature marked as 2, which does not correspond to either plasmon or etalon resonances. The etalon dip in the reflection spectra is marked as E in all the figures. Plasmon resonances corresponding to $N = +1$ and $N = -1$ diffracted orders are marked as +1 and -1 respectively.
5.8. Azimuthal angle dependence

Figure 5.25: Measured white-light reflection spectra from the nano-structured Au/Cu$_2$O interfaces, with a grating periodicity of 280 nm, at different azimuthal angles. (a) $d_{\text{oxyde}} = \sim 166$ nm and (b) $d_{\text{oxyde}} = \sim 232$ nm. The dips in the reflection spectra that are marked with arrows are responsible for the diagonal feature in Fig. 5.24 (a) and (b).

arise from the incomplete oxidation of Cu within the ridges, giving rise to a smaller effective etch depth.

In Fig. 5.24, in addition to the plasmon and etalon dips in the reflection spectra, we can also notice the presence of another resonance which appears as a diagonal line (marked 2). The wavelength at which this resonance occurs is observed to be a function of the azimuthal angle and the thickness of the Cu$_2$O layer. For clarity, the measured reflection spectra for three different azimuthal angles are shown again in Fig. 5.25(a) and (b), for Cu$_2$O thicknesses $\sim 166$ nm and 232 nm respectively. The dips in the reflection spectra that do not correspond to the etalon or plasmon resonances are marked with arrows. For example, for an oxide thickness of 166 nm and $\Lambda = 280$ nm, the resonance occurs at 710 nm at $\phi = 60^\circ$ which moves to 780 nm at $\phi = 20^\circ$ (Fig. 5.25(a)). Similarly at $\phi = 60^\circ$, and oxide thickness of 232 nm (Fig. 5.25(b)), we can see that this extra resonance occurs at a wavelength of 750 nm, which moves to a wavelength of 800 nm at $\phi = 40^\circ$. These azimuthal angles are close to the values at which we observe an absorption peak in the pump laser absorption, and a dip in the emitted THz amplitude in Fig. 5.22 and 5.23.

In Fig. 5.26, the azimuthal-angle dependence of the white-light reflection spectra from nano-structured Au/Cu$_2$O samples with a periodicity of 230 nm is shown. (a) and (b) correspond to the measured reflection spectra for the two oxide thicknesses, 166 nm and 232 nm respectively. The
plasmon modes in the figures are approximately indicated by the dashed lines. The plasmon resonance wavelength, and the strength of the resonance is dependent on the azimuthal angle. After an azimuthal angle of $\sim 50^\circ$, the plasmon resonances are weak and, hence, the dashed line is shown only for values of $\phi$ up to $50^\circ$. When the periodicity of the grating is 230 nm, the plasmon resonance occurs near a wavelength of 800 nm, which is the laser excitation wavelength. The azimuthal-angle dependent dip in the reflection spectra corresponds to a plasmon resonance, but the etalon minimum is independent of the azimuthal angle. When $d_{\text{oxide}} = 250$ nm, the plasmon resonance merges with the etalon dip. For clarity, we also show the 1D graphs for the same data as above in (c) and (d), but only at three different azimuthal angles. Figures (e) and (f) show the calculated azimuthal-angle dependent white-light reflection spectra from the samples of oxide thickness 166 nm and 232 nm respectively. It can be seen that the calculated spectra show good agreement with the measured reflection spectra. The measurements and calculations have so far provided evidence that plasmon excitation is responsible for the enhanced THz emission from nano structured Cu$_2$O/Au interfaces. In the next section, we turn to calculations of the near-field to determine what the local pump fields look like when plasmons aren’t excited.

5.8.3 Near-field analysis

For nano-structured Au/Cu$_2$O samples of grating periodicity 230 nm, the plasmon resonance occurs at a wavelength of 800 nm, when $\phi = 0^\circ$ (Fig. 5.26). In Fig. 5.27, we plot the calculated near-field distributions of the intensity of the pump light of wavelength 800 nm on the samples of oxide thickness 166 nm (171 nm in calculations) and 232 nm (250 nm in calculations). The plotted quantity is $|E(x, z, \lambda)|^2$, as a function of the position in the x-z plane, where $E(x, z, \lambda)$ is the position-dependent, and the wavelength-dependent total electric-field amplitude. For each thickness of the oxide layer (171 nm and 250 nm), two cases are shown, corresponding to azimuthal angles of $0^\circ$ and $90^\circ$. The 800 nm light is incident at an angle of 45° from the top-left side of the figure. At $\phi = 0^\circ$, we observe plasmon-like modes for both 171 nm and 250 nm thick Cu$_2$O samples. There is a strong electric field at the interface of AuCu and Cu$_2$O, which is vertically well-confined, characteristic of surface plasmon polariton modes. At $\phi = 90^\circ$, there is very little field inside the Cu$_2$O thin film, and no features associated with plasmon excitation are seen. Compared to the sample with an oxide thickness of 250 nm, the sample with a 171 nm thick oxide film
Figure 5.26: The experimental and simulated reflection spectra of nano-structured Au/Cu$_2$O thin films of periodicity 230 nm, normalized to the reflection from a bare gold surface and plotted as a function of the azimuthal angle. (a) measured, $d_{\text{oxide}} \sim 166$ nm, (b) measured, $d_{\text{oxide}} \sim 232$ nm, (c) and (d) shows the same data as (a) and (b) for three different azimuthal angles. (d) simulated azimuthal-angle dependent reflection spectra, $d_{\text{oxide}} = 171$ nm (e) simulated, $d_{\text{oxide}} = 250$ nm.
has more light reflected from the sample, due to etalon effects. The red box surrounding the azimuthal angle values in the figure denotes that plasmon excitation is expected in this case.

The near-field distributions corresponding to a grating periodicity of 280 nm, are shown in Fig. 5.28. For this sample periodicity, the plasmon resonance occurs at a wavelength of 925 nm, and hence at 800 nm wavelength, no features of plasmon excitation are expected. Slight edge-enhancement effects are observed at an azimuthal angle of 0°, since the electric field of the incident light is oriented perpendicular to the ridges.

In Fig. 5.29, we show the near-field cross sections of $|H_y|$ in the x-z plane for the two grating periodicities 230 nm and 280 nm. The excitation of surface plasmons in the case of gratings of periodicity 230 nm, is more clearly visible here. It can be seen that in the case of samples with a periodicity 230 nm, there is a strong localization of the magnetic field at the surface, for both the samples of thickness 171 nm and 250 nm. The asymmetry in the field distribution arises from the non-normal incidence of the pump light. A movie showing the $|H_y|$ distribution as a function of time, for the four different cases shown in Fig. 5.29, is uploaded online and can be seen through this web-link https://www.dropbox.com/sh/kc7xj2tt7dsg0zo/70SXtvJtKm?lst. For the samples with a periodicity of 230 nm, a surface-wave propagating to the left is visible, whereas in the case of samples of periodicity 280 nm, no such surface-wave is observed. This reinforces the argument that plasmons are excited when light of wavelength 800 nm is incident on nano-structured Au/Cu$_2$O samples of grating periodicity 230 nm. For a nano-structured sample of periodicity 280 nm, there is a plasmon at a wavelength of 735 nm, corresponding to the diffracted order $N = +1$. We have also included a movie of the magnetic near-field corresponding to this case. It is to be noted that the the magnetic field shown in the movies is comprised of the incident and reflected light as well as the plasmon field, which makes it somewhat difficult to clearly recognize the plasmons, in the case the plasmons propagates in the same direction as the incident field component along the surface. For comparison, we have also included movies of flat Au/Cu$_2$O interfaces, for two different oxide thicknesses, 171 and 250 nm.

5.9 Conclusion

THz emission from Au/Cu$_2$O interfaces occurs in a region near to the Schottky interface, where the static electric field has a maximum. The absorption
Figure 5.27: The calculated optical near-field cross-sections of nanostructured Au/Cu$_2$O thin films with a grating periodicity 230 nm and thicknesses 171 nm and 250 nm, at azimuthal angles $0^\circ$ and $90^\circ$. The plotted quantity is $|E(x, z, \lambda)|^2$. The wavelength of the incident light is 800 nm in the simulations. The cases where plasmon excitation is expected is denoted by the red box around the value of the azimuthal angle.
Figure 5.28: The calculated optical near-field cross-sections of nanostructured Au/Cu$_2$O thin films with a grating periodicity 280 nm and thicknesses 171 nm and 250 nm, at azimuthal angles 0° and 90°. The plotted quantity is $|E(x, z, \lambda)|^2$. 

\[ \Lambda = 280 \text{ nm} \]
\[ d_{\text{Cu}_2\text{O}} = 250 \text{ nm} \]
\[ d_{\text{Cu}_2\text{O}} = 171 \text{ nm} \]
5.9. Conclusion

Figure 5.29: The calculated magnetic near-field cross-sections of nano-structured Au/Cu$_2$O thin films for grating periodicities 230 and 280 nm and for two oxide thicknesses 171 nm and 250 nm. $\phi = 0^\circ$ in all the cases. The plotted quantity is $|H_y|$ as a function of the position in the x-z plane.
of the pump light further away from the interface does not contribute efficiently to the THz emission. Hence for increasing the THz emission, it is important that the absorption of the laser light takes place near the interface.

We have shown that by nano-structuring the interfaces between Au and Cu$_2$O, we can excite surface plasmons to concentrate pump laser energy at the interface. This leads to an enhanced THz emission compared to a flat Au/Cu$_2$O sample. The evidences for surface-plasmon-enhanced THz emission can be summarized as follows:

- **Periodicity dependence**: The strongest THz emission was obtained from a sample of grating periodicity 230 nm. We have seen from the white-light reflection spectra that the plasmon resonances depend on the grating periodicity, and that a periodicity of 230 nm is suitable for excitation of surface plasmons at 800 nm wavelength, as predicted.

- **Azimuthal angle dependence**: The maximum pump power absorption and THz emission occur when the grating is oriented vertically and the incident laser is p-polarized. This is the orientation suitable for the excitation of the surface plasmons. The azimuthal angle dependence of the THz emission also indicates that concentrating the absorption of the pump laser light at the interface leads to an increase in the efficiency of THz emission. In other words, it is not just the absorption of the laser by the sample that is important, but where it is absorbed.

- **No enhancement at other resonant modes**: This is also seen from the azimuthal angle dependence of THz emission from the sample of periodicity 280 nm, where a peak in the absorption is observed at an azimuthal angle of 45°. However, this does not result in an increased THz emission, but on the contrary, in a decreased THz emission. One reason for this decrease in the THz emission is that a resonant mode is excited, for which the pump light is concentrated away from the interface, thus contributing less to THz emission.

Thus the measurements and calculations clearly show that to maximize THz emission it matters more where the light is absorbed than how much is absorbed. This understanding may lead to new and improved THz emitters.
In this thesis, we have discussed the potential of plasmonics in enhancing the THz emission from metal (Au) thin films, and metal/semiconductor (Au/Cu$_2$O) junctions.

Several reports on THz emission from gold thin films, upon illumination with femtosecond laser pulses, can be found in the literature and are briefly reviewed in Chapter 2. While plasmonics has been used to enhance the THz emission from these films, the different processes which result in THz generation vary, depending on the incident pump laser power and morphology of the thin films used. We studied the THz emission from thin gold films deposited on etched Si gratings, in an attempt to determine the role played by the surface plasmons in THz generation. The interesting result from our experiments is that the THz emission follows a second-order dependence on the incident pump power, when excited by femtosecond laser pulses at the plasmon excitation angle. This is contrary to the higher-order dependence of THz emission on the incident pump power observed by other groups using similar samples, indicating a multi-photon photoelectric effect. Other processes which might be responsible for the THz emission, namely optical rectification by the surface non-linearity, and the photon-drag effect are also discussed in the chapter. It was seen from our experiments that, as the angle of propagation of surface plasmons on the metal surface varies, a small change in the polarization of the THz pulse emitted is observed. More research into this could lead us to an answer on the role of plasmons on the THz emission from bare gold gratings.

Another important part of this thesis covers the THz emission from Au/Cu$_2$O thin film interfaces, when illuminated with femtosecond laser pulses and the role of plasmonics in enhancing the THz emission from them. Cu$_2$O thin films were fabricated by depositing a thin film of Cu on a suitable substrate and then oxidizing it in the ambient atmosphere.
To understand the oxidation process, we showed in chapter 3, that THz transmission spectroscopy can be used to measure the oxidation kinetics of copper thin films evaporated on silicon substrates. The transmission of broadband THz pulses from 1 to 7 THz through the copper films was measured during oxidation in the ambient atmosphere, at elevated temperatures ranging from 120 - 150 °C. The change in the transmitted THz electric field was correlated with the growth of the cuprous oxide layer and a decrease in the thickness of the copper layer. We also showed that the THz conductivity of evaporated metal thin films depends on the film thickness, due to percolation effects.

Metal/semiconductor interfaces can form a Schottky barrier potential at the interface, creating an electric field. Photo-excited charge carriers, generated near the interface, are accelerated by this electric field and give rise to the emission of THz radiation. However, it has been reported in the literature that Au films deposited on Cu$_2$O form ohmic junctions, and not Schottky junctions. In chapter 4, we show that our Au/Cu$_2$O samples which emit THz radiation, are in-fact AuCu/Cu$_2$O interfaces, due to the formation of a thermal diffusion alloy AuCu. The alloy enables the formation of a Schottky barrier electric field near the interface, which is very important for THz emission from these samples. The formation of this AuCu alloy layer is confirmed by X-ray diffraction measurements, ellipsometry and visual inspection. From the ellipsometry measurements, we also determined the frequency-dependent complex refractive-indices of the Cu$_2$O and AuCu layers.

The capability of Au/Cu$_2$O thin films as broad-band terahertz emitters, can be exploited further by enhancing the THz emission through plasmonics. In order to excite surface plasmons at the metal/semiconductor interface, gold nano-gratings were fabricated and then covered by Cu$_2$O. The evidence for surface-plasmon-enhanced THz emission is obtained from THz emission measurements, as a function of grating periodicity and azimuthal angle. Visible-light reflection-spectroscopy was used to determine the plasmon resonance wavelengths. The experimental results suggest that for increasing the THz emission, it is important that the absorption of the laser light takes place near the interface. This makes sense, as the Schottky electric field is also maximum near the metal/semiconductor interface and decreases as we move away from the interface. Excitation of other resonant, non-plasmonic modes may result in an increased absorption of the pump laser pulses, but not necessarily in increased THz emission, as the pump light may get concentrated away from the interface. Our results are promising in that they give meaning to the motto "more with less": The ex-
citation of surface plasmons gives rise to strong THz emission even though the total amount of material is small compared to other types of emitters. It is possible that this will lead to new applications in THz science and technology.
Surface plasmon dispersion relation on a planar interface

The derivation of surface-plasmon dispersion relation given below can be found in [74] and is partly reproduced here for convenience.

Let us consider a plane interface between two media with frequency-dependent dielectric functions $\varepsilon_1$ and $\varepsilon_2$. We choose the interface to coincide with $z = 0$ axis, as shown in Fig. A.1. $s$-polarized light has its electric field only parallel to the surface of the material and hence cannot induce surface charges. $p$-polarized light has an electric field component perpendicular to the surface of the material and hence is capable of exciting SPP modes. Hence we will consider only $p$-polarized incident light in this derivation. The fields in the two media for a $p$-polarized wave propagating in the $x$-direction along the interface can be written as:

$$
H_1 = (0, H_{y1}, 0)e^{i(k_xx + k_{z1}z - \omega t)}
$$

$$
E_1 = (E_{x1}, 0, E_{z1})e^{i(k_xx + k_{z1}z - \omega t)}
$$

Figure A.1: Schematic illustration of the interface between the two media along which the surface plasmon propagates. The wave vectors $k_{z1}$ and $k_{z2}$ has components along the $x$- and $z$-directions.
$H_2 = (0, H_{y2}, 0)e^{i(k_x x - k_{zz} z - \omega t)}$

$E_2 = (E_{x2}, 0, E_{z2})e^{i(k_x x - k_{zz} z - \omega t)} \quad (A.2)$

By applying Maxwell's equation

$$\nabla \times \vec{H} = \epsilon \frac{\partial \vec{E}}{\partial t} \quad (A.3)$$

we obtain

$$E_{x1} = \frac{k_{z1}}{\epsilon_1 \omega} H_{y1}$$

$$E_{x2} = -\frac{k_{z2}}{\epsilon_2 \omega} H_{y2} \quad (A.4)$$

At the interface between the two materials, we can apply the boundary conditions that the components of the electric and magnetic fields parallel to the interface must be continuous across the interface, when there is no free current at the interface. Hence we can write,

$$E_{x1} = E_{x2}$$

$$H_{y1} = H_{y2} \quad (A.5)$$

From Eq. A.4 and A.5 we can obtain

$$H_{y1} - H_{y2} = 0$$

$$\frac{k_{z1}}{\epsilon_1 \omega} H_{y1} + \frac{k_{z2}}{\epsilon_2 \omega} H_{y2} = 0 \quad (A.6)$$

In order to obtain a solution to the above equations, the determinant has to be zero.

$$\frac{k_{z1}}{\epsilon_1} + \frac{k_{z2}}{\epsilon_2} = 0 \quad (A.7)$$

Further, from Eq. A.4

$$k_{x1}^2 = \epsilon_1 \left(\frac{\omega}{c}\right)^2 - k_{z1}^2$$

$$k_{x2}^2 = \epsilon_2 \left(\frac{\omega}{c}\right)^2 - k_{z2}^2 \quad (A.8)$$
Since the x-component of the wave vector has to be continuous at the interface, from Eq. A.7 and A.8 we can write

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

\[ k_{zi} = \frac{\omega}{c} \sqrt{\frac{\epsilon_i^2}{\epsilon_1 + \epsilon_2}} \quad i = 1, 2 \quad (A.9) \]

Let us assume that medium 1 is a dielectric and medium 2 is a metal with a complex permittivity. Metals have a negative real part for its permittivity and if the absolute value of the permittivity of the metal is higher than that of the dielectric, we can see that \( k_x \) will have a real part. This means that a surface wave propagating in the x-direction is possible. Also, \( k_{z1} \) and \( k_{z2} \) becomes imaginary, which indicates that the field are maximum at the interface and decays exponentially in both z-directions, which is the characteristic of surface plasmon waves.


My experience of doing a PhD can be compared to a rollercoaster ride: it was exciting, adventurous and there were several ups and downs on the way. To reach the end of this journey successfully, I have been graciously helped by a lot of people. It is my pleasure to remember those people and thank them in these pages.

First and foremost I am grateful to Prof. Paul Planken for his guidance throughout my PhD. I have learnt quite a lot from the scientific discussions with him and also enjoyed plenty of freedom as a researcher. Many thanks to Paul for reading and correcting the thesis patiently and for having oriented and supported my research through uncertain moments.

I am also sincerely grateful to Dr. Aurèle Adam, for his continuous help during my PhD. He often had clever solutions to technical problems in the lab, and I also gained a lot through discussing my research with him. I also thank Aurèle for performing the simulations that complemented my experimental work which gave the finishing touch to the work presented in my thesis.

Let me also thank our head of the department Prof. Paul Urbach, for the support and encouragement he provided.

I would like to thank all the committee members for their time and effort in reading my thesis and providing suggestions.

I am grateful to Yvonne van Aalst for always expertly solving problems regarding administrative stuff, she is of great help to students who have to go through residence permit and visa issues. I also thank Mandy Jungschlager and Lucia Heijenga-Becht for their help with the paper work.

I sincerely thank Gopakumar Ramakrishnan for helping me get familiarized with the lab. I am also indebted to him for generously spending time in training me at the nanofacility, and for all the constructive discussions we had. It has been a pleasure to work with Nishant Kumar, and he was always
ready to help in the lab or in the nanofacility. I remember with gratitude the help of Joseph Knab in the initial stages of my PhD. Gerward Weppelman was a cheerful lab-mate during his master thesis period and I thank him for the good times at the lab. I am also indebted to him for translating the summary of this thesis and the propositions accompanying it.

Peter Petrik is an expert in the field of ellipsometry and my sincere thanks to Peter, for assisting me with the ellipsometry modeling involved in this thesis and for suggesting changes to my thesis after reading it carefully. I thank Ruud Hendrikx from the Department of Material Science and Engineering, for the X-ray diffraction measurements of many samples, and his readiness to answer my questions on the analysis. Thanks to Peter Swart from DIMES technology center for his valuable help with I-V curve measurements. I also thank Carel Heerkens from the Charged Particle Optics group, for his help in the nano-facility, whose suggestions and recipes helped me considerably in the nanofabrication. He also helped a lot with wet etching of silicon, although that work is not mentioned in this thesis. My thanks to Lei Wei for listening enthusiastically about my stories related to research and for the discussions we had. I also thank Thim Zuidwijk, Rob Pols and Roland Horsten for the technical support they gave.

I am indebted to Marco van der Krog, Marc Zuiddam, Roel Mattern, Anja van Langen, Hozanna Miro, Charles de Boer and Arnold van Run for their valuable help at the nanofacility. I would also like to thank Marco and Charles specifically for training me to use the electron-beam pattern generator and the reactive ion etcher respectively.

I thank Omar El Gawhary for being always ready to help academically and otherwise. Special thanks to Nandini Battacharya for being supportive at all times. I am also grateful to Silvania Pereira, Florian Bociort, Aura Nugrowati, Prof. Joseph Braat and Jeffrey Meisner for their help. I thank Peter Somers and Willeke for being patient listeners whenever I wanted to try my expertise of Dutch language during Optica events. I also thank Reshmi Chakkitakandy for her warm response whenever I approached her for some help.

My colleagues in Optica have been a great source of support throughout. In an incredibly international group, thank you all for making me feel perfectly at home. It was great to have office-mates like Pascal van Grol, Thomas Liebig, Olaf Janssen, Sarathi Roy, Daniel Asoubar, Edgar Rojas Gonzàles, Peter Petrik and Sven van Haver. Let me thank (in no particular order at all) Alberto da Costa Assafraõ, Alessandro Polo, Man Xu, Mounir Zeitouny, Luca Cisotto, Andreas Hänssel, Mahsa Nemati, Morris Cui, Axel
Wiegmann, Katsiaryna Ushakova, Adonis Reyes Reyes, and Wouter Westerveld for being wonderful colleagues and friends. Let me also thank the new faces of Optica: Daniel Nascimento Duplat, Zhe Hou, Ying Tang, Matthias Strauch, Yifeng Shao and Hamed Ahmedpanahi for the good times. It was also a pleasure to work with Wioletta Moskaluk, Rik Starmans, and Hui-Shan Malisa Chan. I also thank the several students who did their master/bachelor thesis in Optica for adding to the ‘gezelligheid’ of the group. Several of you have also participated in discussions related to my research, sat through my presentations and have given your valuable opinions and ideas, for which also I thank you. I also thank Eda Kuran, Elisabetta Iorfida, Emanuelle Prest, Manish Kumar, José-Luis Alatorre Warren and Dinesh Lokanathan for your friendship and for making my stay in the Netherlands more interesting. I thank Venkatesh Sheshan for keeping me informed about the bureaucratic procedure surrounding the PhD defense. Thanks to Wouter Westerveld and Olaf Janssen for giving me the latex template used for this thesis. I sincerely thank Andreas and Nishant for accepting the role of paranymphs at my thesis defense.

Finally I acknowledge and thank the help of my family through their constant support in every possible way. I am immensely grateful to my father Ramanandan Manhapra and mother Rajeswari Kottayi Pilappara. It’s their hardwork and sacrifices, which gave me the foundation to do this PhD. I will thank my sisters Parvathi, Oormila and Uthara for their love and encouragement and the confidence they have in me. Everyday, I miss terribly the fun we have when we are together. Lastly, I thank my husband Nitish for being there for me always. This thesis would not have been possible without your help in more than one way and thank you for everything.

Gopika Ramanandan Kottayi Pilappara, March 2014
About the Author

Gopika Ramanandan Kottayi Pilappara was born in 1987 in Kozhikode, India. In 2009 she completed a five-year integrated MSc degree in Photonics from the Cochin University of Science and Technology, India, with distinction. Her master thesis was on the behavior of carbon nanotubes in an optical trap for which she worked at the Tata Institute of Fundamental Research, Mumbai, India. In September 2009, she moved to Delft, to do a PhD at the Optics Research Group of Delft University of Technology. Her PhD position was funded by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) and the Stichting voor Technische Wetenschappen (STW). Her work has been presented at several international conferences and published in refereed journals.

Refereed Journal Publications

G. K. P. Ramanandan, A. J. L. Adam, and P. C. M. Planken Plasmonic nano-gratings for enhanced THz emission from Schottky junction thin films (manuscript in preparation)

G. K. P. Ramanandan, G. Ramakrishnan, A. J. L. Adam and P. C. M. Planken Generation of terahertz light from nano-structured metal surfaces (manuscript in preparation)


N. Kumar, P. Petrik, G. K. P. Ramanandan, O. El Gawhary, S. F. Pereira, W. M. J. Coene, and H. P. Urbach, Experimental demonstration of coherent Fourier scatterometry for sub-wavelength features reconstruction and nano-positioning of periodic structures (submitted)

G. Ramakrishnan, N. Kumar, G. K. P. Ramanandan, A. J. L. Adam, R. Hendrikx and P. C. M. Planken, Plasmon-enhanced terahertz emission from a semiconductor/metal


Conference Contributions

G. K. P. Ramanandan, A. J. L. Adam and P. C. M. Planken, Plasmon enhanced terahertz emission using nano-gratings, Physics@FOM Veldhoven, Veldhoven 2014 (oral).

G. K. P. Ramanandan, A. J. L. Adam and P. C. M. Planken, Plasmonic gratings for enhanced terahertz emission from metal-semiconductor thin films, The 38th International Conference on Infrared, Millimeter and Terahertz waves (IRMMW-THz), Mainz, 2013 (oral).


G. K. P. Ramanandan and P. C. M. Planken, THz transmission spectroscopy to study the oxidation kinetics of nanometer thick copper films, The 36th International Conference on Infrared, Millimeter, and Terahertz waves (IRMMW-THz), Houston, 2011 (oral).

G. R. Kottayi Pilappara, G. Ramakrishnan and P. C. M. Planken, Oxidation kinetics of nano-scale copper thin films using terahertz transmission spectroscopy, Physics@FOM Veldhoven, Veldhoven 2011 (oral).

