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Emission of terahertz pulses from nanostructured metal surfaces

G K P Ramanandan, G Ramakrishnan¹, N Kumar¹, A J L Adam and P C M Planken

Faculty of Applied Sciences, University of Technology Delft, Lorentzweg 1, 2628 CJ Delft, The Netherlands
E-mail: p.c.m.planken@tudelft.nl

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Abstract
When (nanostructured) metals, such as gold and silver, are illuminated with laser pulses having a duration in the femtosecond range, they can emit pulses of THz light. Most of these experiments have been performed using amplified lasers, giving rise to energy densities on the sample on the order of mJ cm⁻². The results of the different experiments are surprisingly inconsistent in both the measurements of the THz fluence as a function of laser fluence and in the interpretation of the results. This paper reviews the current state of affairs of this interesting topic and discusses some effects related to surface preparation that may influence the emission THz light on metals, particularly silver and copper. We also show results of measurements on nanostructured metals using unamplified laser pulses, which emphasize the role played by plasmons in the generation of THz light. When increasing the optical energy density on a specially nanostructured sample, we observe a transition from a 'classical' second-order non-linear optical process to a higher-order process as the source of the THz radiation. This supports recent results on a differently structured metal by Polyushkin et al (2014 Phys. Rev. B 89 125426), who also observe two different power regimes when decreasing the intensity coming from the high energy density side.

Keywords: terahertz emission, metals, nanostructures, metal gratings

(Some figures may appear in colour only in the online journal)

1. Introduction
Terahertz (THz) radiation, electromagnetic radiation with frequencies ranging from roughly 10¹¹ to 10¹³ Hz, has many applications in science and technology (Mittleman 2003, Sakai 2005), such as far-field imaging (Hu and Nuss 1995, Rutz et al 2006, Adam et al 2009), near-field imaging (Bitzer et al 2009, Kumar et al 2012, Huber et al 2008) and spectroscopy (Cheville and Grischkowsky 1999, Jepsen et al 2007, Chakkittakandy et al 2010, Johnston et al 2003, Knab et al 2013). Of all the techniques capable of generation and detecting THz radiation, THz time-domain spectroscopy (THz-TDS) is one of the most powerful. In THz-TDS a femtosecond pump laser pulse generates a single- or few-cycle THz pulse in a suitable non-linear optical material and a synchronized, weaker probe laser pulse detects the electric field of the THz pulse as a function of time. The advantage of measuring the electric field is that both the phase and amplitude of the THz electric field are measured and, thus, both the absorption and the refractive index of a material can be determined. The corresponding frequency bandwidth of a single- or few-cycle pulse is very large and can span several decades in frequency. In fact, frequencies over 70 THz have been generated using sub-10 fs laser pulses (Sell et al 2008). Many different materials have been used to generate THz pulses and the number of physical processes known to be capable of generating THz radiation has grown over the years. Popular methods to generate THz pulses include photoconductive switches, (Van Exter and Grischkowsky 1990, Zhao et al 2002), optical rectification in non-linear optical crystals, (Zhang et al 1992, Nahata et al 1996, Hebling et al 2008, Chakkittakandy et al 2008), the photo-Dember effect at semiconductor surfaces (Kono et al 2000, Gu et al 2002, Johnston et al 2002), and generation in air (Cook and Hochstrasser 2000, Dai et al 2011). The majority of these processes are second-order non-linear optical processes and...
some, particularly generation in air, are third-order processes in which two photons within a laser pulse with a central frequency $\omega$ are mixed with a photon of another pulse with central frequency $2\omega$ to generate a photon in the THz frequency range.

2. THz emission from (nanostructured) metal surfaces: an overview

In recent years, a number of results have been published on the emission of THz pulses from a remarkable new set of sources: (non-magnetic) metal surfaces. The first reports were from Kadlec et al (Kadlec et al 2004, Kadlec et al 2005), who reported on the emission of THz pulses from flat silver and gold surfaces upon illumination with intense optical pulses from an amplified Ti : sapphire laser (energy density $\sim 8 \text{ mJ cm}^{-2}$). They observed a second-order dependence of the THz fluence on pump power at high excitation fluences, becoming higher-order for lower excitation fluences. For silver, a surprising fifth-order power dependence was observed. In their experiments on gold layers, they were unable to produce THz radiation from layers thinner than about 100 nm. They explained this by ballistic transport of electrons from the excitation side of the film to the glass side, where carrier accumulation leads to a field opposing the initial current, which strongly weakens the emitted THz pulse. For cancellation to occur the transport time of the carriers needs to be short, on the order of the laser pulse duration or shorter, so that the currents are reduced within the pulse duration. The authors proposed that this could explain why emission from samples thinner than 100 nm was not observed.

A few years later, in 2007, Welsh et al published a paper on THz emission from gold-coated glass gratings having a period suitable for the excitation of surface plasmon polaritons, or surface plasmons for short (Welsh et al 2007). By using intense optical pulses from an amplified Ti : sapphire laser, they saw THz emission from these nanostructured metal surfaces only for p-polarized pump light with a strong peak when the angle of incidence of the pump was such that surface plasmons were excited. The pump energy density in their experiments reached values up to $3.5 \text{ mJ cm}^{-2}$. Little THz emission was observed for s-polarized incident pump light for which no surface plasmons were excited. Plasmon excitation was also inferred from the increased pump-absorption around the angle of incidence where plasmon excitation was expected. One highly interesting feature of their measurements, shown in figure 1, is that the THz fluence showed a strong dependence on pump fluence. For many, if not most, THz emitters the THz fluence shows a quadratic dependence on pump fluence. In their case, the THz fluence as a function of incident pump energy density followed a power law with an exponent of 3.5, decreasing to a value of about 2 at higher powers. For comparison, they also showed the THz fluence as a function of incident pump energy density for a conventional ZnTe emitter, fitting this to a power law with an expected exponent of about 2. To explain their results, they used a model in which multi-photon excitation of the metals leads to the creation of free electrons near the surface of the metal (Irvine and Elezzabi 2006), followed by the acceleration of photoexcited electrons in the ponderomotive potential (Boot and Harvie 1957), which is associated with the evanescently decaying electric field of the surface plasmon (see also Welsh and Wynne 2009). Since the work function of gold is around 5.3 eV, at least four 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, which is due to the modification of the potential by the laser field and the resulting tunnelling of photoelectrons out of the metal (Tóth et al 1991).

Ramakrishnan and Planken reported on the emission of THz pulses after illuminating a discontinuous layer of only $\sim 8 \text{ nm}$ of gold with $800 \text{ nm}$ wavelength, 50 femtosecond pulses from a Ti : sapphire laser oscillator, providing an energy density of $\sim 10^{-3} \text{ mJ cm}^{-2}$ at the surface (Ramakrishnan and Planken 2011). Gold, when deposited on a material like glass, first forms nano-islands when deposition begins. These nano-islands coalesce into more complicated networks as deposition continues and it finally form a continuous layer for an average thickness larger than about 10 nm. The threshold average thickness where the individual networks become a single, large conducting fractal-like network is called the percolation threshold. The THz emission as a function of average layer thickness, shown in figure 2, was reported in their paper to reach a maximum just above the percolation threshold and above the average layer thickness where the maximum in the absorption occurred, which is also shown in the figure. The reason for the increased emission is the excitation of localized surface-plasmon intensity hot spots in the percolating metallic thin film, resulting in enhanced fields and in enhanced optical rectification of the incident femtosecond laser pulses. In contrast to the results of Welsh et al (Welsh and Wynne 2009), which were discussed above, they observed a second-order non-linear process as the source of the THz emission, and not a higher order process. They suggested that (localized) surface plasmons played an important role in the THz emission since the electric field of a plasmon is strongest at the metal surface.

![Figure 1. Measured THz fluence as a function of incident energy density, emitted by a ZnTe crystal (blue dots) and by a Au grating on glass (dark-red dots). The blue solid line is a linear fit to the ZnTe data points. The red solid line is a fit to the Au grating data points for energy density values lower than 1.9 mJ cm$^{-2}$. Adapted from: Welsh et al (2007), Welsh and Wynne (2009).](image-url)
and the THz emission seems to occur through the surface $\chi^{(2)}$ of the sample. The emitting dipole was assumed to be perpendicular to the surface because the polarity of the THz emission was found to change sign while changing the angle of incidence from $+45^\circ$ to $-45^\circ$.

Experiments on metallic gratings were also reported by Garwe et al (Garwe et al 2011) and Schmidt et al (Schmidt et al 2012), who measured the THz emission from gold gratings on a fused silica substrate upon illumination with femtosecond, amplified pump laser pulses with energy densities on the metallic grating of $\sim$3.5 mJ cm$^{-2}$. In contrast to the experiments performed by Welsh et al (Welsh et al 2007, Welsh and Wynne 2009), they used thermal detection of the emitted THz radiation using a superconducting transition edge sensor. They claimed that plasmon excitation and ponderomotive acceleration of electrons in the evanescent plasmon field cannot explain their results since they also observed emission of THz light from the fused silica/gold interface, making electron emission a less likely explanation. Instead, they proposed an in-plane current as the source of the THz emission, although no clear mechanism for the creation of the unidirectional current was given. Curiously, they measured a linear dependence of the THz fluence on pump laser fluence. This is somewhat unusual since the known THz emission processes are usually second or higher order processes in which the THz fluence depends on the square, or on a higher power, of the pump fluence.

In 2011 Polyushkin et al (Polyushkin et al 2011) published results on THz emission from silver and gold nanoparticle arrays, and from percolating silver films using high power laser pulses from an amplified Ti : sapphire laser. They measured a power law dependence for the metal particles and the thin film with an exponent of 1.5 and 1.75, respectively. The bimodal power dependence (exponent 5–6 at lower power, lower exponent at high power) is consistent with the model based on ponderomotive acceleration of the photo-generated electrons because ultrafast photo-emission measurements have also shown such bimodal power dependencies (Gloskovskii et al 2008). 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, then 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 (Irvine and Elezzabi 2006).

In a very recent report (Polyushkin et al 2014), the authors discuss the results of extended measurements on silver nanohole arrays in which they show how the THz energy depends on the laser intensity to the power 1.4 at low fluences, increasing to 3.7 at high intensities. According to these authors, these measurements show the transition from an intensity regime where regular, surface related second-order optical rectification dominates to a regime where acceleration of photoexcited electrons in the evanescent field of plasmons is responsible for the emission. For the nanoparticles, the lower order process was not observed. Interestingly they also measured the energy of the emitted electrons as a function of pump fluence. At high pump intensities they observe a strong correlation with the THz fluence, providing additional support for the acceleration of photoexcited electrons as the source of the THz light. These results thus confirm and expand on the results by Welsh et al (Welsh et al 2007, Welsh and Wynne 2009).

Suvorov et al (Suvorov et al 2012) also performed measurements of THz emission from non-structured, essentially flat gold, copper and aluminum surfaces, illuminated using femtosecond laser pulses from an amplified Ti : sapphire laser. They detected the emitted THz light using a bolometer. They observed an exponential dependence of the emitted THz fluence on laser power. It should be noted that the energy density in their experiments ranged from 10 to 80 mJ cm$^{-2}$, which is considerably higher than the values reached in all the other experiments described above. In their paper they explain the generation of THz light by an in-plane current, which results from non-linear mixing of the surface electric charge induced at the metal surface, and the tangential electric field of the pump laser pulse.

Another type of nanostructured metal surface was used by Kajikawa et al (Kajikawa et al 2012), who showed how gold nanospheres with a diameter of about 80 nm that are immobilized on the surface of a gold substrate by an aminoundecanethiol self-assembled monolayer emit THz pulses when illuminated with laser pulses from a Ti : sapphire oscillator. In the experiment, they found that the THz fluence depends quadratically on laser fluence and they attributed this to a $\chi^{(2)}$ surface optical non-linearity.
Second-order THz generation was also observed by Ramakrishnan et al (Ramakrishnan et al 2012) after the excitation of surface plasmons on a 42 nm thick continuous gold film, in the so-called Kretschmann geometry. In this geometry, a gold film is evaporated on a glass prism and illuminated from the glass side to excite surface plasmons. Apart from the natural roughness of such a film, a 42 nm gold film forms a continuous layer. Their results showed that it is possible to generate THz radiation from continuous gold films thinner than 100 nm. The THz fluence depended on the square of the optical fluence indicating a second-order non-linear optical process as the source of the THz radiation.

A different kind of optical excitation of a metal was recently used by Dai and Zhang (Dai and Zhang 2014). They used a two-colour pump consisting of phase-locked laser pulses at central frequencies $\omega$ and $2\omega$ to generate THz radiation from thin gold films on a sapphire substrate. This process is quite similar to generation of THz radiation in air (Cook and Hochstrasser 2000, Dai et al 2011) and thus relies on the third-order non-linear susceptibility of the metal, with the THz fluence scaling linearly with the fluence in the beam having frequency $2\omega$, and quadratically with the fluence of the beam at frequency $\omega$. Such an excitation scheme has the advantage that THz pulses can also be generated at perpendicular incidence since the asymmetry, which is needed for the creation of a net THz polarization, is provided by the fields of the combination of the two beams and not by an asymmetry that is intrinsic to the sample itself.

3. Factors influencing THz emission

3.1. Pump energy density

It is quite remarkable that the experiments briefly described above mostly do not agree on the mechanism responsible for the THz emission from metal surfaces. In addition, when the emitted THz fluence depends on the incident laser fluence through a power law, then the different experiments show an astonishing number of exponent values, ranging from 1 to 6! The experiments of Suvorov et al (Suvorov et al 2012) even show an exponential dependence. It is, of course, not a priori impossible that different generation mechanisms are at work, which would explain why different exponents are found. In fact, as already pointed out by Ramakrishnan et al (Ramakrishnan et al 2012) and observed by Polyushkin et al in their most recent paper (Polyushkin et al 2014), part of the difference may be found in the different optical power regimes reached in the different experiments. The attainable power density in experiments using amplified Ti:sapphire lasers is many orders of magnitude higher than those in experiments using Ti:sapphire oscillators. A high intensity makes the emission of electrons from a metal much more likely than a low intensity, for which conventional surface-induced second-order non-linear optical processes may dominate. Still, not all of the differences can be explained by this and the reasons for the differences are hard to find. The current state of this interesting topic in THz science does, however, allow us to shed some light on effects that may influence the generation of THz light from (nanostructured) metal surfaces. At the very least, researchers should be aware of these effects so that they can be ruled out as sources of THz radiation in future experiments on metal surfaces.

3.2. Surface contamination

One of the effects that may influence the generation of THz light from (nanostructured) metal surfaces is contamination of the metal surface. For example, as mentioned in some of the papers discussed above, silver surfaces are susceptible to contamination with sulfide compounds. In ambient air, traces of H$_2$S can react with silver surfaces to form Ag$_2$S. Pollutants, in general, can change the workfunction of a metal; that is, the energy needed to free an electron from the metal. In addition, even single molecular layers can substantially enhance second-order THz emission from metal surfaces (Ramakrishnan et al 2012), perhaps drowning out signals from other generation mechanisms. When Ag$_2$S forms on a Ag surface, THz emission can become much stronger due to the fact that Ag$_2$S is a semiconductor and Ag$_2$S/Ag forms a Schottky interface with a corresponding static electric depletion field. Such interfaces can emit THz light when the semiconductors absorbs pump light, thus optically creating free carriers that are subsequently accelerated in this static field (Zhang et al 1990). When the metal is deposited on the semiconductor, the emission from such a system is generally weak. When the semiconductor is deposited/formed on the metal, the THz emission from such an interface may be significant (Ramakrishnan et al 2013). An example of this is shown in figure 3, where we plot the measured THz electric field as a function of time emitted by a 100 nm silver layer exposed to low concentrations of H$_2$S, illuminated with 50 fs pulses from a Ti:sapphire oscillator. The signal is significant and larger than the THz fields emitted from bare gold surfaces or percolated gold surfaces. In general, no THz emission was observed from a freshly prepared, clean, silver layer for the typical energy densities of $\sim 10^{-3}$ mJ cm$^{-2}$ used. This means that the silver sulfide is required to observe THz emission. No effort was made to measure the exact thickness of the sulfide layer because this measurement was performed as a proof-of-principle experiment only, although we want to point out that similar signals were also obtained from silver layers that had been exposed to laboratory air for only a couple of weeks. Without information on the way samples were treated, it is difficult to conclude whether these effects contribute to the THz signals from silver surfaces that are shown in various papers.

3.3. Enhanced absorption by extremely thin dielectric layers

One reason why these effects may sometimes be underestimated is because one naively expects the absorption of such a thin layer to be small. In reality, the absorption may be significant. In an approximation where the metal is a perfect reflector giving a $\pi$ phaseshift in the pump field upon reflection, an absorbing semiconductor layer with a thickness corresponding to a quarter wavelength (inside the semiconductor) would act like an anti-reflection coating, keeping and absorbing most of
in the atmosphere. Absorption and re-emission of THz light by water vapour molecules in the atmosphere.

Figure 3. Measured THz electric field as a function of time emitted by a thin Ag$_2$S layer formed by partial sulfidation of a 100 nm Ag layer. The oscillations to the right of the main pulse are caused by absorption and re-emission of THz light by water vapour molecules in the atmosphere.

Figure 4. Schematic illustration of coherent optical absorption giving rise to increased THz emission. A thin semiconductor layer on a metal acts as its own anti-reflection coating, giving rise to significantly more light absorption, both in the semiconductor and in the metal. For a non-perfect metal, the semiconductor thickness where maximum absorption occurs is much lower than for a perfect metal.

The light inside the semiconductor (figure 4). In reality, metals are not perfect metals and the semiconductor layer can act like an impedance matching layer, allowing more light to enter the metal. One consequence of this is that the phase shift of the pump light upon reflection from the metal/semiconductor interface is no longer π. This can shift the whole curve of pump reflection versus layer thickness into the metal, so that a minimum reflection does not occur for a layer thickness equal to a quarter wavelength but is already present for thinner layers. Dramatic examples of this are the almost 100% absorption at 400 nm wavelength for a 5 nm a-Si layer thickness on silver, and the 95% absorption at 800 nm for a 7 nm thick layer of Ge on gold. It is highly unlikely, of course, that these materials are to be found on the metal surfaces by accident, but it shows that the absorption of light for thin layers of materials on a metal surface may be significantly higher than expected (Kats et al 2013). Ramakrishnan et al (2013).

A similar argument holds for copper surfaces. Cuprous oxide naturally forms on the surface of copper when exposed to air. Cuprous oxide/Cu interfaces are Schottky interfaces that are formed between the naturally formed p-type cuprous oxide and the copper. In fact, we have recently shown that cuprous oxide/metal interfaces are remarkably good THz emitters when illuminated with 50 fs pulses from a Ti : sapphire laser oscillator (Ramakrishnan et al 2013). Plasmon excitation further enhances the emission of THz light from a thin cuprous oxide layer on the surface of a metal (Ramakrishnan et al 2014). This happens because both the plasmon field and the static Schottky depletion field, where the THz signal is generated, are maximum near the metal surface, making significant THz emission from thin layers possible. It is important to realize that, after chemical removal of cuprous oxide from a copper surface, measurable amounts of THz radiation are again observed after exposure to air for just a couple of hours (see also Ramanandan et al (2012)). What is worse, for layers of copper with thicknesses ranging in the tens to hundreds of nanometres on a substrate with a bad thermal conduction, laser heating actually increases the speed of oxidation. Again, without proper information on how the copper surfaces were treated, it is impossible to judge whether these effects contribute to the emission of THz light from the copper surfaces discussed by Suvorov et al (Suvorov et al 2012).

4. Low power excitation

Almost all of the experiments described above were performed at high energy densities >1 mJ cm$^{-2}$. For this reason, it is worthwhile to look into the possibility of using relatively weak femtosecond laser pulses from a Ti : sapphire oscillator to generate THz pulses from nanostructured surfaces. Therefore, in the remainder of this paper we will present the results of THz emission from gold gratings using 50 fs pulses from a Ti : sapphire laser oscillator. We will focus on the role played by surface plasmons in the THz emission and show results of the wavelength dependent optical transmission from gold-on-glass gratings, as well as the wavelength dependent optical reflection from gold-coated gratings etched in Si, illustrating at what wavelengths plasmons are excited. We investigate the importance of plasmon excitation by measuring the electric field of the emitted THz pulses while we vary the pump-power and the azimuthal-angle of the sample. Finally, we also show a measurement of THz emission as a function of laser power from a sandwich structure of gold/glass/percolated gold, which illustrates that, by clever design of the sample, highly non-linear THz generation is attainable using relatively low power laser pulses. Our measurements thus approach the high power regime from the low power side in much the same way as the results from Polyushkin et al (Polyushkin et al 2014) approach the low power regime from the high power side.

Note that this paper focuses exclusively on non-magnetic metals (see for example: Hilton et al (2004)). This was a deliberate decision since the generation mechanisms in materials such as Ni en Fe are usually different from those of the non-magnetic metals such as Ag and Au. We feel that the extra explanations and discussions would make an already long paper even longer. Besides, the generation of THz light by magnetic metals is a topic that deserves its own, separate paper.

The remainder of this paper is organized as follows: due to the important role that surface plasmons can play in the generation of THz radiation from metal surfaces, we first give an introduction on the properties of surface plasmons
and how they can be excited using gratings. We then show optical transmission and reflection spectra, demonstrating that plasmons can be excited at the appropriate wavelengths, followed by results on the generation of THz pulses from these gratings as a function of grating etch depth and azimuthal angle, using unamplified laser pulses from a Ti:Sapphire laser oscillator. Finally, we show the results of a preliminary experiment on a sandwich structure of percolated gold, glass and bulk gold, in which we observe strongly non-linear generation of THz radiation as a function of pump laser power.

5. Surface plasmons

Surface plasmons are charge density oscillations that propagate along the interface of a metal and a dielectric, with coupled electromagnetic fields that decay exponentially away from the interface in both the metal and the dielectric. A schematic representation of the surface charge density and the electric field of the surface plasmon polariton is shown in figure 5. 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 (Zayats et al 2005, Schaadt et al 2005). This field enhancement can effectively enhance several linear and non-linear optical processes, such as second-harmonic generation, SERS, fluorescence, absorption, etc. (Schaadt et al 2005, Simon et al 1974, Steuwe et al 2011). The field enhancement property of plasmons has also been used to increase the performance of devices such as detectors, sensors, and solar cells (Knight et al 2011, Homola 2008).

Surface plasmons are characterized by the solutions of Maxwell’s equations that are localized at the interface of a metal and a dielectric. If we consider the waves that propagate in the x direction (see figure 5), it is possible to solve the wave equation to get a propagating transverse magnetic (TM) mode. The electric field of the surface plasmons can be described as

\[ E_j = (E_{j,x}, 0, E_{j,z})e^{i(k_j x + k_{j,z} z - \omega t)} \quad j = 1, 2, \]  

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. \( k_j \) 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 (Raether 1988, Novotny and Hecht 2006)

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

(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 \( k_j \) to be real. From equation (2), this condition is satisfied if the sum and product of the dielectric functions are either both positive or both negative.

In addition, the normal component of the wave vector in both media is

\[ k_{j,z} = \frac{\omega}{c} \sqrt{\frac{\epsilon_j}{\epsilon_1 + \epsilon_2}}, \quad j = 1, 2. \]  

(3)

Since the wave is confined to the interface, \( k_j \) 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 equation (3). Hence, the condition to have waves confined to the interface becomes

\[ \epsilon_1(\omega)\epsilon_2(\omega) < 0, \]  

(4)

and

\[ \epsilon_1(\omega) + \epsilon_2(\omega) < 0. \]  

(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 have 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 of the materials forming the interface can also have an imaginary part of the dielectric function (Gawhary et al 2014). This leads to $k_z$ also having an imaginary part, leading to the damping of surface plasmons propagating along the interface.

6. Grating coupling of surface plasmons

The dispersion relation of surface plasmons at a metal/dielectric interface, is plotted schematically in figure 6. The solid black line represents the dispersion relation given in equation (2), where, for simplicity and illustration purposes, we have used only the real part of the dielectric permittivity of the metal, which has two branches. The high frequency branch does not represent true surface waves because $k_z$ 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

The dashed line represents the light line in air, $\omega = ck_z$, 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 used excites 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 (Raether 1988). Another method to excite surface plasmons is to use gratings, which is the technique that we will describe in this section. 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

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

(6)

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

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

(7)

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 figure 7. The red lines represent the dispersion of the 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 the sake of 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 $k_{inc,x} = 0$, then 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 $90^\circ$, then 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 $0^\circ$ and $90^\circ$, the direction of propagation of the surface plasmons for the two cases is schematically shown in figures 7(b) and (c).

6.1. 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 figure 8. The plasmon coupling condition given in equation (7) 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 (Chen 2007)

$$k_{SPP}^2 = k_0^2 \sin^2 \theta + N^2 k_g^2 \pm 2N k_{SPP} \sin \theta \cos \phi,$$

(8)

where $k_0$ is the wave-vector of light in free space, $\omega = ck_0$, $\omega_{inc}$ is the frequency of the incident light, $\Lambda$ is the grating period, and $N$ is the order of diffraction.
Figure 7. (a) The grating coupling of surface plasmons is illustrated. The $x$-component of the incident light ($k_{inc,x}$) is shown by the dashed grey line. The scattering of the incident light by the grating results in the lines $k_{inc,x} + k_g$ and $k_{inc,x} - k_g$. 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 $k_{SPP}$ and $-k_{SPP}$. From the figure, it can be seen that surface plasmons can be excited for two frequencies $\omega_{+1}$ and $\omega_{-1}$. (b) and (c) show the direction of propagation of the surface plasmons for the two excitation light frequencies $\omega_{-1}$ and $\omega_{+1}$, respectively. $\theta$ is the angle of incidence of the exciting light with respect to the normal to the metal surface.

where $\theta$ is the angle of incidence of the light beam and $\phi$ is the azimuthal angle (see figure 8). 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 figure 8, 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

$$\Psi = 90^\circ - \arccos\left(\frac{k_g \sin \phi}{k_{SPP}}\right).$$  \hspace{1cm} (9)

7. THz emission from gold gratings

Inspired by the various experiments described in literature on the emission of THz light from metal surfaces illuminated with femtosecond laser pulses, we performed THz emission experiments with plasmonic metal gratings. Our goal was to determine the role played by surface plasmons in THz generation. Our initial experiments were performed using a commercially obtained etched grating on quartz, similar to that used by Welsh et al (2007). 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 used to promote the adhesion between the Au and the quartz substrate. From the plasmon-excitation condition given in equation (7), we can calculate that, for this periodicity, a plasmon resonance should appear at an angle of $36^\circ$.

To confirm that we can excite plasmons on this grating, we have performed white-light transmission spectroscopy measurements. An Ocean Optics fibre-coupled spectrometer was used to measure the spectral transmission using a tungsten–halogen lamp as a white-light source. The zeroth-order transmission spectra of the light through the grating sample were measured for different angles of incidence. The measurements were 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 figure 9. 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 (Ebbesen et al. 1998, Ghaemi et al. 1998). At an angle of incidence of 36°, a resonance is observed at a wavelength of 800 nm, confirming the excitation of surface plasmons in the THz generation experiment.

The small period of the grating (500 nm in this case), means that there is no second-order or higher-order diffraction in the wavelength range where we performed the reflection experiments. First-order diffraction may show up as a decrease in the transmitted or reflected zeroth-order light as a function of wavelength because the wavelength is lowered to just below the wavelengths where a plasmon is observed. The reason for the decrease is that diffraction into the first order leads to reduced power in the zeroth order. In fact, hints of this are clearly visible in figure 9 (and in figure 12, to be discussed later). However, our aim is to look for a plasmon resonance peak which can clearly be identified, and we therefore did not bother to correct for the extra loss of energy in the zeroth order due to diffraction of light into the first order.

The experimental setup used for the THz generation and detection is shown in figure 10(a). The laser source used in the experiments described in this section is a Ti : Sapphire oscillator (Femtosource XL80, Femtolasers) with an average power of 800 mW, 50 fs pulse duration, and a centre 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°, which is the angle at which we expect plasmon excitation to take place. The maximum energy density on the sample was 0.02 mJ cm⁻². 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 (1 1 0) ZnTe crystal of 500 μm thickness. The probe beam is also focused onto the ZnTe crystal through an aperture in the second parabolic mirror. The polarization of the probe beam is modified by the electric field of the THz pulse inside the ZnTe crystal. The change in the polarization of the pump beam is measured using a combination of a quarter-wave plate, a Wollaston prism, and a differential detector.

In figure 10(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°. The pulse emitted when the metal grating grooves are oriented perpendicular to the p-polarized incident laser pulses is in red, corresponding to an azimuthal angle \( \phi = 0° \). When \( \phi = 90° \), 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. Figure 10(d) shows the measured electric-field amplitude of the THz pulses 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. We note that this is the first time that THz emission has been observed from a metallic grating using laser pulses from a Ti : Sapphire oscillator. The pump energy density at the grating is some 10⁴ times lower than in the case of excitation with pulses from an amplified Ti : Saphire laser.

### 7.1. 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 figure 11(a). In figure 11(b), the blue line shows the percentage 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 \( \phi = 0° \) we observe a peak in the absorption. The THz emission is correlated with the absorbed laser power (see figure 11(b)): the amplitude of the emitted THz pulse also sharply decreases as the azimuthal angle is changed from 0°, and at 90° 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. The strong enhancement of the THz emission when plasmons are excited is consistent with a picture in which the source of the THz emission lies at, or close to, the surface, where the electric field of a surface plasmon is also the strongest.

Equation (8) shows that, in principle, higher-order modes may also give rise to the excitation of surface plasmons. For example, for $N = 2$ (taking the plus sign in equation (8)) and $\phi = 60^\circ$, plasmons can be excited for incident wavelengths of around 800 nm. However, figure 11 shows no clear sign of additional absorption around $\phi = 60^\circ$. The most likely explanation for this is that, in this case, plasmon excitation is simply not very efficient. Note that, in general, plasmon excitation is typically most efficient when the incident electric field is perpendicular to the grating lines.

7.2. Etch depth dependence

Since it is easier to perform the experiment for an angle of incidence of 45°, we also fabricated gratings with a periodicity suitable for plasmon excitation at 45°. 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 a wavelength of $\sim 1100$ nm, and also because the Au layer is 100 nm thick, transmission spectra could not be obtained for these samples. In figure 12(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 to 60 nm. The spectra are normalized to the reflection spectrum of a bare Au surface. It can be seen that at 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 corresponds to Wood’s anomaly (Maystre 2012). 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 happens because the diffraction intensity depends on the etch depth of the grating (Raether 1988).
Figure 11. (a) Azimuthal-angle dependence of the pump laser reflection (red) and transmission (black) through the gold grating sample. (b) The pump laser absorption (blue) and the THz emission (black) as a function of the azimuthal angle. A grating azimuthal angle $\phi = 0^\circ$ corresponds to an orientation where the grating lines are perpendicular to the table.

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 measured electric field of the emitted THz pulses is plotted in figure 12(a). 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 observation of THz emission.

7.3. s-polarized pump

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. By using low power laser sources, a second-order THz generation process from gold thin films has been observed, but only for the case of percolated-gold by Ramakrishnan and Planken (2011) and for the case of a thin film of continuous gold (Ramakrishnan et al 2012) using similar pump powers. The emitting THz dipole in these cases was assumed to be along the surface normal. 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 on an Au grating, we fabricated another grating of periodicity 1090 nm, which was suitable for exciting surface plasmons at an angle of incidence of 45$^\circ$ and an azimuthal angle of 90$^\circ$. The white-light reflection spectra of this grating for different azimuthal angles and s-polarized incident lights are shown in figure 13. It can be seen that the plasmon resonance wavelength depends strongly on the azimuthal angle. When $\phi = 102^\circ$, the plasmon resonances seen at $\sim 700$ nm and $\sim 1 \mu$m correspond to the plasmons excited through the grating vectors $\pm k_x$. When $\phi = 90^\circ$, the surface plasmons excited from both $\pm k_x$ approach each other. The THz pulse emitted from this sample oriented at an azimuthal angle of 90$^\circ$, when excited with s-polarized pump laser pulses, is shown in figure 14. 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 be easily 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. The physical mechanism responsible for the generation of an
s-polarized THz electric field component is currently under investigation.

8. THz emission from a percolated gold sandwich structure

So far, the THz emission that we have seen in our experiments from (nanostructured) metal surfaces scaled quadratically with laser fluence. This is in sharp contrast with most experiments using amplified laser pulses, which often observe higher order emission. As has been suggested before (Ramakrishnan et al 2012), these observations need not be in contradiction with each other since experiments with Ti : Sapphire oscillators have a high repetition rate, allowing the use of sensitive lock-in detection techniques that facilitate the detection of THz pulses generated by second-order non-linear optical processes.

Figure 14. THz emission from a metal grating of periodicity 1090 nm. The experimental conditions are: $\theta = 45^\circ$, $\phi = 90^\circ$, and the incident pump laser is s-polarized.

Figure 13. The white-light reflection spectra of the gold-grating with a periodicity 1090 nm, for different azimuthal angles 90°, 94°, 98° and 102°, and s-polarized incident light, at $\theta = 45^\circ$.

s-polarized THz electric field component is currently under investigation.

If the low pump power regime can be reached using amplified laser pulses, then how can the high power regime be reached using low power pulses from a Ti : Sapphire oscillator? One way to achieve this would be to decrease the laser spot size on the sample, thus increasing the intensity. However, for spot sizes smaller than a few hundred micrometres diameter, THz radiation is emitted in all directions and not everything can be collected. A different approach is to improve the coupling of pump light to a metallic surface. To achieve this, we have fabricated a sample consisting of 10 nm of (percolating) gold, on 127 nm of SiO₂, on top of a thick 100 nm gold layer. This sandwich structure (see inset of figure 15) shows remarkably strong extinction of >90% in a large bandwidth. When illuminated with laser pulses from an 11 MHz rep. rate, 50 fs, 800 mW average power Ti : Sapphire laser, visible damage to the sample occurs within minutes, presumably because of melting. For this reason, the sample was rotated along the surface normal with several thousand revolutions per minute, reducing the heat load on a particular spot considerably. The sample was illuminated off-centre and visible damage began to manifest itself only after about an hour, which leaves enough time to measure the THz electric field. In figure 15, we plot preliminary results of measurements of the THz amplitude generated by this sample as a function of incident average laser power. This figure shows that at average laser powers less than about 100 mW, the THz amplitude scales quadratically with incident pump power. For incident average laser powers larger than 100 mW, the THz amplitude (power) also follows a power law but with an exponent of 2.5 (5).

We caution, however, that different samples give different values for the exponent, ranging from 1.5 to 2.5, when plotting the THz amplitude versus incident laser power. The reason for these differences may be related to slightly different optical properties from sample to sample and to the fact that the experiments take place close to the damage threshold of the samples. Regardless, exponent values larger than 1 are consistently obtained for large enough average laser powers, showing that the non-quadratic regime is attainable, even with the relatively low pulse energy density of a Ti : Sapphire oscillator of $\sim 10^{-3}$ mJ cm$^{-2}$, which is some three to four orders of magnitude lower than what is used in experiments with amplified laser pulses.
The generation of THz light by the illumination of (nanostructured) metals with femtosecond pulses is an interesting topic containing elements of optics and solid state physics. Based on the results that can be found in literature and based on our own results, it seems clear that there is no single explanation for all of the results at all energy densities, and perhaps not even for all of the different kinds of metals that have been tested so far. Nevertheless, two important conclusions can be drawn. The first conclusion and, perhaps, the most obvious one is that there seem to be two different laser pump power regimes giving rise to two different generation mechanisms. At low power, $\sim 10^{-5}$ mJ cm$^{-2}$, a second-order non-linear optical process appears to be responsible for the THz emission. At high power, $> 1.0$ mJ cm$^{-2}$, a highly non-linear process (i.e. the acceleration of photoexcited electrons by the plasmon evanescent field) dominates. A transition region between the two regimes has recently been observed, both using high power and low power lasers. At high energy densities, the exponent of the power law describing the relation between the THz fluence and the energy density is often lower. This may perhaps be explained by saturation effects. It could be that this is the cause of the linear dependence between the THz fluence and the pump fluence observed by Garwe et al. Note that one should be careful when comparing energy densities, especially for nanostructured surfaces because nanostructures have the ability to locally enhance the field. In other words, the local intensity might be higher than expected. Even flat surfaces are not really flat and unintentionally nanostructured metal surfaces (grains) might give rise to locally strong fields and to higher-order THz emission.

The second conclusion is that it is very important to have clean metals and to clearly state how the surface of the metal has been treated. This is especially true for the metals copper and silver, which can oxidize and sulfidize, giving rise to Schottky contacts that can efficiently emit THz light upon illumination with femtosecond laser pulses. However, it is difficult to see how this would give rise to an exponential power dependence (Suvorov et al.). Nevertheless, it is important to be aware of these effects since they may give rise to a power law dependence with an exponent of 2. Extremely thin layers of material might also change the workfunction of a metal and this could affect the observed exponent value in the power law dependence. It is currently unclear whether this plays a role (one can speculate whether the laser pulses may even clean the surface), although it might explain the various exponent values observed in high power laser experiments.

It is clear that a wealth of physics is to be found in the generation of THz light from metal surfaces and future experiments may focus on methods to increase the output and on trying to better identify the different factors that can influence the emission. There may still be many surprises in store for us in the future.

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