Investigation of plasmonic response of metal nanoparticles to ultrashort laser pulses

Submitted by
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I certify that all material in this thesis which is not my own work has been identified and that no material has previously been submitted and approved for the award of a degree by this or any other university.
I lovingly dedicate this thesis to all my family, especially to my wonderful wife Yulia, who fills my life with joy and happiness; to my father Konstantin, mother Irina and sister Daria who have always provided me with their unconditional love and support through the years; to my grandparents Gennady and Nina and my aunt Ekaterina who with my parents have brought me up in love and care; and in memory of my dear grandparents Ivan and Nadezhda.
In this thesis the interaction of ultrashort laser pulses with metal nanostructures is investigated via two different phenomena: coherent acoustic oscillations of nanoparticles and generation of THz pulses on metal surfaces.

Both of these effects rely on the collective oscillations of free conduction electrons in metal surfaces, plasmons. The field of plasmonics gained a great interest in the last twenty years due to the unique properties of these surface modes. It is the effects of the resonant response of plasmonic structures to incident electromagnetic wave, in particular, in visible and infrared bands and the concentration of the electromagnetic field in small subwavelength regions with significant enhancement of the incident field that make plasmonics so attractive for various applications, such as biochemical sensing, enhanced fluorescence, surface-enhanced Raman scattering, and second harmonic generation, amongst others.

Investigation of the coherent particle vibrations is performed using the pump-probe technique which allows measurement of the transient transmission signals. The expansion and subsequent contraction of the nanoparticle following the ultrashort laser pulse excitation lead to a shift of the plasmon band which can be traced by transient spectroscopy. We have investigated the effect of the particle thickness on the frequency of the fundamental vibrational mode. In addition, we measured the vibrational particle response during the particle shape deformation, both symmetrical and asymmetrical.

Exploration of the THz generation phenomena on plasmonic structures was performed using THz time-domain spectroscopy, the method which allows tracing of the generated THz field in the time-domain. We were able for the first time to measure the THz pulses generated from arrays of metal nanoparticles. Our observations verify the role of the particle plasmon mode in the generation of THz pulses. In addition, by exploring the dependence of the THz emission on the femtosecond pulse intensity we showed a high nonlinearity in the THz generation mechanism. The experimental results were assessed in the context of a recently proposed model where the THz radiation is generated via the acceleration of the ejected electrons by ponderomotive forces.
To reveal another proposed mechanism of the THz generation from plasmonic structures, namely optical rectification, we investigated the THz generation and electron emission from the arrays of nanoparticles and nanoholes. Our results suggest that both mechanisms may contribute to generation of THz pulses from the same sample under different illumination conditions.

In addition to periodic arrays of nanoparticles and nanoholes, THz generation from random metal-dielectric films was investigated. The microstructuring of such films allowed selective THz frequency generation which was explained by a model of dipole THz emitters. In addition, the effects of low temperature and pressure on the THz generation efficiency were investigated.
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<tr>
<td>SPP</td>
<td>Surface plasmon polariton</td>
</tr>
<tr>
<td>LSPR</td>
<td>Localised surface plasmon resonance</td>
</tr>
<tr>
<td>TIR</td>
<td>Total internal reflection</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>SMF</td>
<td>Semicontinuous metal film</td>
</tr>
<tr>
<td>FEM</td>
<td>Finite element method</td>
</tr>
<tr>
<td>FDTD</td>
<td>Finite-difference time-domain</td>
</tr>
<tr>
<td>PP</td>
<td>Pump-probe</td>
</tr>
<tr>
<td>THz-TDS</td>
<td>THz time-domain spectrometer</td>
</tr>
<tr>
<td>OR</td>
<td>Optical rectification</td>
</tr>
<tr>
<td>EOS</td>
<td>Electro-optic sampling</td>
</tr>
<tr>
<td>SERS</td>
<td>Surface-enhanced Raman spectroscopy</td>
</tr>
<tr>
<td>SHG</td>
<td>Second harmonic generation</td>
</tr>
<tr>
<td>THG</td>
<td>Third harmonic generation</td>
</tr>
<tr>
<td>EBL</td>
<td>Electron beam lithography</td>
</tr>
<tr>
<td>NSL</td>
<td>Nanosphere lithography</td>
</tr>
<tr>
<td>AR NSL</td>
<td>Angle-resolved nanosphere lithography</td>
</tr>
<tr>
<td>TBF</td>
<td>Transmitted bright-field</td>
</tr>
<tr>
<td>RBF</td>
<td>Reflected bright-field</td>
</tr>
<tr>
<td>TDF</td>
<td>Transmitted dark-field</td>
</tr>
<tr>
<td>RDF</td>
<td>Reflected dark-field</td>
</tr>
<tr>
<td>NA</td>
<td>Numerical aperture</td>
</tr>
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<td>TTM</td>
<td>Two-temperature model</td>
</tr>
<tr>
<td>Abbreviation</td>
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<tr>
<td>--------------</td>
<td>-------------------------------------------------</td>
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<tr>
<td><strong>RIE</strong></td>
<td>Reactive-ion etching</td>
</tr>
<tr>
<td><strong>ET</strong></td>
<td>Etching time</td>
</tr>
<tr>
<td><strong>PEEM</strong></td>
<td>Photoemission electron microscopy</td>
</tr>
<tr>
<td><strong>MPPE</strong></td>
<td>Multiphoton photoemission</td>
</tr>
<tr>
<td><strong>NSOM</strong></td>
<td>Near-field scanning optical microscopy</td>
</tr>
<tr>
<td><strong>EF</strong></td>
<td>Enhancement factor</td>
</tr>
<tr>
<td><strong>TOF</strong></td>
<td>Time-of-flight</td>
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Chapter 1
Background physics

This Chapter summarizes some of the main facts about surface and particle plasmon polaritons. Starting with the differential form of Maxwell’s equations, and using averaged parameters of the material, we derive the dispersion relation of volume plasmons. To describe the properties of metals we introduce a Drude model which treats metals as a free electron gas. Then the dispersion of the surface-plasmon polariton (SPP) waves at a metal/dielectric interface is given in a general form, and also for Drude metals. The properties of the volume and surface plasmon modes are discussed, followed by a brief introduction to the excitation techniques of SPPs. To find out the response of metal particles we present the solution of Laplace’s equation in spherical coordinates. By applying appropriate boundary conditions to the solutions we arrive at expressions for the particles response in the electrostatic approximation. The Chapter is finished by discussing the effects of field enhancement in the vicinity of metal particles at their resonances, one of the main effects of nanoplasmonics.

1.1 Maxwell’s equations

The macroscopical Maxwell’s equation in the media may be written in the form [1]

\[
\begin{align*}
\text{div} D &= \rho_{\text{ext}}, \\
\text{div} B &= 0, \\
\text{rot} E &= -\frac{\partial B}{\partial t}, \\
\text{rot} H &= \frac{\partial D}{\partial t} + J_{\text{ext}}.
\end{align*}
\]  

These equations link the macroscopic fields \( D, E, B \) and \( H \) with the external densities of charge and current. The fields are called respectively the displacement field, the electric field, the magnetic field and the induction field. Each pair of the fields \( D \) and \( E \), and \( B \) and \( H \) may be further linked by means of polarization \( P \) and magnetisation \( M \), electric and magnetic dipole moments per unit volume inside the media, respectively. These fields describe the reaction of the media to the external fields.

\[
D = \varepsilon_0 E + P, \quad H = B/\mu_0 - M,
\]  

\[ \tag{1.2} \]
where the parameters $\varepsilon_0$ and $\mu_0$ are so called electric permittivity and magnetic permeability of the vacuum, respectively. Since we deal only with non-magnetic materials, we do not need to consider the field $\mathbf{M}$. Moreover, we consider only linear and isotropic media in which in the frequency domain the following constitutive relations may be written

$$
\mathbf{D}(\mathbf{k}, \omega) = \varepsilon_0 \varepsilon(\mathbf{k}, \omega) \mathbf{E}(\mathbf{k}, \omega), \quad \mathbf{B}(\mathbf{k}, \omega) = \mu_0 \mu(\mathbf{k}, \omega) \mathbf{H}(\mathbf{k}, \omega)
$$

(1.3)

Here $\mathbf{k}$ is the wave vector and $\omega$ is the angular frequency. Often it is possible to ignore the spacial dispersion, then the material parameters $\varepsilon$ and $\mu$ are only functions of the angular frequency $\omega$. Ignoring the spatial dispersion means that the response of the material to the external fields is local, i.e. does not depend on the fields at other points in the media. Further, the polarization $\mathbf{P}$ is linked with the electric field through the relation

$$
\mathbf{P} = \varepsilon_0 \chi \mathbf{E},
$$

(1.4)

where $\chi$ is the electric susceptibility. The relation (1.4) leads to a link between susceptibility and dielectric permittivity by $\varepsilon = 1 + \chi$.

The microscopic response of the media to the external field can be described by either complex permittivity function $\varepsilon = \varepsilon' + i\varepsilon''$ or complex refractive index $n = n + i\kappa$, where $\kappa$ is known as the extinction coefficient. At optical frequencies the refractive index may be determined by, for example, an investigation of the reflection from the material. The permittivity then may be found from the relation $\varepsilon = n^2$, which leads to the following expressions

$$
\varepsilon' = n^2 - \kappa^2, \quad \varepsilon'' = 2n\kappa,
$$

$$
n^2 = \left(\varepsilon' + \sqrt{\varepsilon'^2 + \varepsilon''^2}\right)/2, \quad \kappa = \varepsilon''/2n.
$$

(1.5)

The extinction coefficient $\kappa$ determines the absorption of light in the material. It is linked to the absorption coefficient $\alpha$ in Beer-Lambert law $I(\chi) = I_0 e^{-\alpha x}$ via the relation

$$
\alpha(\omega) = 2\kappa(\omega) \omega/\varepsilon
$$

(1.6)

After establishing the link between the electric field and the displacement field, the combining of the relation (1.3) with Maxwell’s equations (1.1) in the case of nonmagnetic media without sources leads to the wave equation

$$
\text{rot rot} \mathbf{E} = -\mu_0 \frac{\partial^2 \mathbf{D}}{\partial t^2},
$$

(1.7)
which after applying the Fourier transform

\[ E(k, \omega) = \int E(r, t) e^{i(k \cdot r - \omega t)} \, dr \, dt \]  

(1.8)
can be rewritten in the form

\[ k^2 E(k, \omega) - k(kE(k, \omega)) = \varepsilon(k, \omega) E(k, \omega) \frac{\omega^2}{c^2}. \]  

(1.9)
The solutions of the equation (1.9) may be divided into two classes depending on the polarization of the electric field vector. For transverse waves, where the wave vector and the electric field vector are orthogonal to each other \( kE(k, \omega) = 0 \), the solution of the equation (1.9) leads to the following dispersion relation

\[ k^2 = \varepsilon(\omega, k) \frac{\omega^2}{c^2} \]  

(1.10)
For longitudinal waves, for which \( E \parallel k \) the solution (1.9) gives the relation

\[ \varepsilon(k, \omega) = 0, \]  

(1.11)
which means that longitudinal oscillations are only possible at the frequencies when the dielectric permittivity equals zero.

1.2 The Drude model

To describe the metals, an analytical form of the dielectric permittivity as a function of the frequency is required. The model which relies on the approach of free electron gas to describe the optical properties of the metal is called the Drude model. In this model the movement of electrons in the external electromagnetic field \( E \) is described by the equation

\[ m^* \ddot{x} + m^* \gamma \dot{x} + eE = 0. \]  

(1.12)
Here \( m^* \) is the effective mass of electron and \( \gamma \) is the parameter, which describes dissipation of electron kinetic energy through scattering on other electrons and phonons, \( \gamma = 1/\tau \), where \( \tau \) is called the relaxation time, which is of order of 10 fs for noble metals at room temperature. If the monochromatic external field \( E(t) = E_0 e^{-i\omega t} \) is applied, then the solution of the equation (1.12) has the form

\[ x(t) = \frac{E_0}{m^* (\omega^2 + i\gamma \omega)} E(t). \]  

(1.13)
The displacement of electrons with the number density \( n_0 \) causes the appearance of the macroscopic polarization

\[
P = -n_0 \varepsilon_0 \mathbf{E} = -\frac{n_0 \varepsilon_0^2}{m^* (\omega^2 + i \omega \gamma)} E. \tag{1.14}
\]

From the relations (1.4) and (1.14) the susceptibility can be written in the form

\[
\chi = -\frac{n_0 \varepsilon_0^2}{\varepsilon_0 m^* (\omega^2 + i \omega \gamma)}. \tag{1.15}
\]

The dielectric permittivity can be found then as \( \varepsilon = 1 + \chi \)

\[
\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i \omega \gamma} = 1 - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2} + i \frac{\omega_p^2 \tau}{\omega(1 + \omega^2 \tau^2)}, \tag{1.16}
\]

where

\[
\omega_p = \sqrt{\frac{n_0 \varepsilon_0}{\varepsilon_0 m^*}} \tag{1.17}
\]

is the plasma frequency of the free electron gas, which is an eigenfrequency of the system of free electrons. In the case of negligible damping, \( \omega \gamma \ll 1 \), the dielectric constant is predominantly real and the relation (1.16) takes the form

\[
\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}. \tag{1.18}
\]

It should be noted that the Drude model describes only the system of free electrons and thus fails to explain more complex effects such intraband transitions of electrons. This effect may be described phenomenologically by introducing a background dielectric permittivity \( \varepsilon_\infty \) in (1.16):

\[
\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i \omega \gamma}. \tag{1.19}
\]

### 1.3 Volume and surface plasmons

With the properties of the metal suitably described, we can find the dispersion relation of the traveling wave in the metal by substituting the expression for dielectric permittivity (1.18) into (1.10)

\[
\omega = \sqrt{\omega_p^2 + c^2 k^2}. \tag{1.20}
\]
The oscillations which satisfy the equation (1.20) are called *volume plasmons*. Since the dielectric permittivity is always positive for \( \omega > \omega_p \), the volume plasmons exist in the region of the metal transparency. Another feature of the volume plasmons is that they are not localized oscillations, because their wavelength is bigger than the light wavelength in free space. The properties of volume plasmons can be studied by *electron energy-loss spectroscopy* [2], which is used to determine the absorption spectra of metals and evaluate their plasma frequencies. More interesting types of the plasmon oscillations appear at the interface of metal and dielectric, they are called *surface plasmons*. The properties of these oscillations may be derived from the equation (1.7) by assuming no external electrical charges \((\text{div}\, \mathbf{D} = 0)\). The equation may be written for each of the media with slow spatially varying dielectric permittivity and harmonic time dependence of the electric field in the form of the Helmholtz equation

\[
\nabla \times \nabla \times \mathbf{E} + \omega^2 \varepsilon \mathbf{E} = 0, \quad (1.21)
\]

where \( \omega = \omega/c \) is the *wave number* of the light in free space.

The simplest geometry that may sustain a surface-plasmon polariton is the interface between a metal with dielectric function \( \varepsilon_1(\omega) \) and an insulator with positive real dielectric constant \( \varepsilon_2 \). The in-plane wave vector \( k_x \) of this oscillation is connected with the frequency \( \omega \) by a dispersion relation \( \omega(k_x) \). By using the boundary conditions: the continuity of normal component of vector \( \mathbf{D} \), and the continuity of the tangential component of vector \( \mathbf{H} \), the solution of equation (1.21) takes form [1]

\[
k_{zz}/k_{z1} = -\varepsilon_2/\varepsilon_1, \quad (1.22)
\]

where \( z \) direction is perpendicular to the surfaces interface. From this relation it follows that a surface wave requires \( \text{Re}[\varepsilon_1] < 0 \) if \( \varepsilon_2 > 0 \). This condition is satisfied for dielectrics and metals which have negative the real part of \( \varepsilon_1 \) at frequencies below the bulk plasma frequency \( \omega_p \), as it is follows from (1.16). Additionally to relation (1.22) the momentum conservation law written for the incident light requires
\[ \varepsilon_j \left( \frac{\omega}{c} \right)^2 = k_j^2 + k_{2j}^2, \quad j = 1, 2. \]  

Relations (1.22) and (1.23) combined together give the dispersion relation \( \omega(k_x) \) which is the central result of this section.

\[ k_x = \frac{\omega}{c} \left( \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right)^{1/2}, \]

\[ k_{2j} = \left[ \varepsilon_j \left( \frac{\omega}{c} \right)^2 - k_x^2 \right]^{1/2} = \frac{\omega}{c} \left( \frac{\varepsilon_2^2}{\varepsilon_1 + \varepsilon_2} \right)^{1/2}, \quad j = 1, 2. \]

Figure 1.1 represents dispersion relation (1.24). SPP dispersion curve never crosses the light dispersion line. Therefore free-propagating light cannot couple directly to surface plasmons. Different techniques may be used to overcome this momentum mismatch, which are described in the next section.

For real \( \omega \) and \( \varepsilon_2 \) and \( \varepsilon_1'' < \varepsilon_1' \), we obtain a complex \( k_x = k_x' + ik_x'' \) with

\[ k_x' = \frac{\omega}{c} \left( \frac{\varepsilon_1' \varepsilon_2}{\varepsilon_1' + \varepsilon_2} \right)^{1/2}, \quad k_x'' = \frac{\omega}{c} \left( \frac{\varepsilon_1' \varepsilon_2}{\varepsilon_1' + \varepsilon_2} \right)^{3/2} \frac{\varepsilon_1''}{2(\varepsilon_1')^2}. \]

Figure 1.1. Dispersion relation of volume plasmons in metal (black solid line) and SPP at the metal/dielectric interface (red solid line). The metal is assumed lossless. The dotted line represents dispersion relations of light in air.
The dispersion curve of surface plasmons has two different regions: at the low frequencies (mid-infrared or lower) this curve is tangent to the light line so the surface plasmon propagation constant $k_x$ is close to $k_0$ at the light line. In the region of large wave-vectors, the frequency of surface plasmons approaches the characteristic surface plasmon frequency

$$\omega_{sp} = \omega_p \sqrt{1 + \varepsilon_2}, \quad (1.27)$$

as can be shown by inserting the free-electron dielectric function (1.18) into (1.24).

To estimate the confinement of the plasmon field we calculate the spatial extension and propagation length of the SPP field. Wave vectors $k_{x2}$ and $k_{x1}$ are imaginary due to the relations $\omega/c < k_x$ and $\varepsilon_1' < 0$ (see (1.25)), so that the field amplitude of the SPPs decreases exponentially as $\exp(-|k_x||z|)$, normal to the surface. The depth at which the field falls to $1/e$, equals

$$\delta_j = \frac{1}{|k_j'|} = \frac{\lambda}{2\pi} \left( \frac{\varepsilon_1' + \varepsilon_2'}{\varepsilon_2'} \right)^{1/2}, \quad j = 1, 2 \quad (1.28)$$

For $\lambda = 600$ nm one obtains for silver $\delta_{x2} = 390$ nm and $\delta_{x1} = 24$ nm, and for gold 280 nm and 31 nm, respectively [3].

The propagation length of SPPs can be found by seeking the imaginary part $k''_x$ of the complex surface plasmon wavevector, see (1.26)

$$\delta_{sp} = \frac{1}{2k_x''} = \frac{\lambda}{2\pi} \left( \frac{\varepsilon_1' + \varepsilon_2'}{\varepsilon_2'} \right)^{2/3} \left( \frac{\varepsilon_1''}{\varepsilon_1'} \right)^2 \quad (1.29)$$

For silver which has the lowest losses in the visible spectrum, propagation distances are typically in the range 10 – 100 µm, increasing up to 1 mm at wavelength near to 1.5 µm.

### 1.4 Excitation of SPP

As stated above, there is the difficulty to excite SPPs by light because of the dispersion relation lies beyond the light line ($k_x > \omega/c$). In order to transform the photon with frequency $\omega$ into SPP one should increase the wave-vector of the
photon $h\omega/c$ by $\Delta k_x$. There are many techniques for SPP excitation by light, by means of prisms, gratings, highly focused optical beams and nanostructured near-fields, amongst others [1, 4]. In this section we describe prism coupling of light to SPP.

The prism coupling technique is based on frustrated total internal reflection (TIR), which was proposed by Otto [5] in 1968. In this method the light before impinging on the metal surface has its in-plane momentum increased by passing through the prism with dielectric constant $\varepsilon_p > \varepsilon_0$, the dielectric constant of the insulator between the metal and prism. The sketch of the structure geometry is shown in Figure 1.2a. The light can excite SPP if its in-plane momentum equals the momentum of SPP, which in turn is higher that the momentum of the free-space photon at the same frequency, i.e. $\omega c_p \sin \theta / c > \omega c_0 \sin \theta / c$. The latter leads to the relation for incident angles $\sin \theta > (\varepsilon_0 / \varepsilon_p)^{1/2}$. This requirement according to Snell’s law means illumination at angles higher than angles of TIR on the prism-insulator interface, which leads to strong attenuation of transmitted wave. Thus the distance between the prism and metal has to be less than the light wavelength.

![Figure 1.2. Prism coupling of SPP using frustrated TIR in Otto (a) and Kretschmann (b) configurations.](image)

The insulator and metal may be interchanged in the case of thin metal film. The SPPs are excited then by the light transmitted through the metal film at the bottom metal/dielectric interface as shown in Figure 1.2b. This geometry is called Kretschmann [6] configuration and is commonly used. The prism coupling may be used for measuring optical properties of thin metal films. For this
purpose the intensity of the reflected light is scanned over a range of angles. A drop of the reflectivity indicates SPP excitation. Due to momentum matching at the angle of coupling light to the plasmon mode, back conversion from SPP to light occurs as well. The destructive interference between the leakage radiation and the reflected part of incident light determines the minimum in reflected intensity. The films with optimum thickness may provide zero reflection and thus full absorption of incident light [7].

Figure 1.3 shows the experimental data of SPP excitation in silver film in Kretschmann geometry obtained in our measurements. The film is attached to a 45° silica prism with a refractive index $n = 1.46$ by means of index-matched oil. The film is illuminated by a laser of wavelength 632.8 nm and an angle scan is produced by the rotation table.

![Figure 1.3. Excitation of SPP in silver film by using Kretschmann geometry. Black solid line represents our experimental data, the fitting is shown by red dotted line. Retrieved parameters give the thickness $d = 48.4$ nm and the dielectric constant $\varepsilon = -17.22 + 0.61i$.](image)

The intensity of the reflected light drops at an angle at which the in-plane momentum of the light equals the SPP momentum. The width and depth of the curve is determined by the balance of the radiative and non-radiative losses. The data are fitted by the routine based on recursive Fresnel coefficients (the computer program is developed by Baptiste Auguié). The fitting shows good agreement with experiment.
1.5 Localized surface plasmons: mathematical techniques

In this section the Laplace equation in spherical coordinates will be solved by expansion in Legendre polynomials [8]. The solutions then will be used in the next section to find out the response of metal spheres to electrostatic field.

Laplace equation for the electric potential in empty space in Cartesian coordinates is,

$$\Delta \Phi = \frac{\partial^2 \Phi}{\partial x_1^2} + \frac{\partial^2 \Phi}{\partial x_2^2} + \frac{\partial^2 \Phi}{\partial x_3^2} = 0. \quad (1.30)$$

and transforms, when we change coordinates to the spherical polar \((r, \theta, \phi)\).

The old coordinates are linked to the new ones by the following formulas

$$x_1 = r \sin \theta \cos \phi, \quad x_2 = r \sin \theta \sin \phi, \quad x_3 = r \cos \theta. \quad (1.31)$$

The spherical polar coordinates are a curvilinear but orthogonal coordinate system so the length element can be written as

$$dl = h_1^2 dr^2 + h_2^2 d\theta^2 + h_3^2 d\phi^2, \quad (1.32)$$

where \(h_1, h_2, h_3\) are the Lamé parameters which for spherical coordinates are

$$h_1 = \sqrt{\sum_{i=1}^{3} \left(\frac{\partial x_i}{\partial r}\right)^2}, \quad h_2 = \sqrt{\sum_{i=1}^{3} \left(\frac{\partial x_i}{\partial \theta}\right)^2} = r, \quad h_3 = \sqrt{\sum_{i=1}^{3} \left(\frac{\partial x_i}{\partial \phi}\right)^2} = r \sin \theta. \quad (1.33)$$

The Laplacian can be written through the Lamé parameters as

$$\Delta = \frac{1}{h_1 h_2 h_3} \left[ \frac{\partial}{\partial r} \left( h_2 h_3 \frac{\partial}{\partial r} \right) + \frac{\partial}{\partial \theta} \left( h_1 h_3 \frac{\partial}{\partial \theta} \right) + \frac{\partial}{\partial \phi} \left( h_1 h_2 \frac{\partial}{\partial \phi} \right) \right]. \quad (1.34)$$

Thereby, the Laplace equation in the spherical polar coordinates has the form,

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \Phi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Phi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \Phi}{\partial \phi^2} = 0. \quad (1.35)$$

The variables in this equation can be separated and the function \(\Phi(r, \theta, \phi)\) can be sought in the form

$$\Phi(r, \theta, \phi) = F(r)Y(\theta, \phi). \quad (1.36)$$

Then for the function \(F(r)\) we can obtain the Euler equation

$$\frac{d}{dr} \left( r^2 F'(r) \right) - \lambda F(r) = 0 \quad (1.37)$$
Background physics

and

\[
\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} + \lambda Y = 0
\]  
(1.38)

for the function \( Y(\theta, \varphi) \), which are called spherical harmonics and can be represented as

\[
Y(\theta, \varphi) = \Theta(\theta) \Psi(\varphi), \quad \Psi(\varphi + 2\pi) = \Psi(\varphi).
\]  
(1.39)

For the functions \( \Theta(\theta) \) and \( \Psi(\varphi) \) we obtain the equations

\[
\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \Theta'(\theta) \sin \theta \right) + \left( \lambda - \frac{\mu}{\sin^2 \theta} \right) \Theta(\theta) = 0,
\]  
(1.40)

\[
\Psi''(\varphi) + \mu \Psi(\varphi) = 0.
\]  
(1.41)

From the periodicity condition we find that \( \mu = k^2 \), where \( k \) is an integer. Thereby,

\[
\Psi(\varphi) = A \cos k\varphi + B \sin k\varphi.
\]  
(1.42)

In the equation (1.40) we make a change of variable \( \cos \theta = \xi \) and obtain the following equation [8]

\[
\frac{d}{d\xi} \left[ (1 - \xi^2) \frac{d\Theta}{d\xi} \right] + \left( \lambda - \frac{k^2}{1 - \xi^2} \right) \Theta = 0, \quad -1 < \xi < 1.
\]  
(1.43)

This equation is called the generalized Legendre equation, and its solutions are the associated Legendre functions. Consider at first the ordinary Legendre differential equation with \( k^2 = 0 \)

\[
\frac{d}{d\xi} \left[ (1 - \xi^2) \frac{dP}{d\xi} \right] + \lambda P = 0.
\]  
(1.44)

The solution can be represented by a power series of the form

\[
P(\xi) = \xi^\alpha \sum_{j=0}^{\infty} a_j \xi^j,
\]  
(1.45)

where \( \alpha \) is an undefined parameter. Substituting this expression in (1.44) we obtain

\[
\sum_{j=0}^{\infty} \left[ (\alpha + j)(\alpha + j - 1) a_j \xi^{\alpha+j-2} - \left[ (\alpha + j)(\alpha + j + 1) - \lambda \right] a_j \xi^{\alpha+j} \right] = 0.
\]  
(1.46)
In this equation the coefficient of each power of $\xi$ must vanish separately. So we can find

\[
\begin{align*}
& \text{if } a_0 \neq 0, \text{ then } \alpha (\alpha - 1) = 0, \\
& \text{if } a_1 \neq 0, \text{ then } \alpha (\alpha + 1) = 0.
\end{align*}
\]

(1.47)

and for general value of $j$

\[
a_{j+2} = \frac{(\alpha + j) (\alpha + j + 1) - \lambda}{(\alpha + j + 1) (\alpha + j + 2)} a_j.
\]

(1.48)

Our aim is to obtain the solution that converges at $\xi = \pm 1$ so we should demand that the series terminate. For this we need to assume that $\lambda = l(l + 1)$ with $l$ equals zero or a positive integer. The polynomials obtained by this method are called the Legendre polynomials of order $l$, $P_l(\xi)$. Here we give the first few polynomials:

\[
\begin{align*}
P_0(\xi) &= 1, \\
P_1(\xi) &= \xi, \\
P_2(\xi) &= \frac{(3\xi^2 - 1)}{2}, \\
P_3(\xi) &= \frac{(5\xi^3 - 3\xi)}{2}, \\
P_4(\xi) &= \frac{(35\xi^4 - 30\xi^2 + 3)}{8}.
\end{align*}
\]

(1.49)

There is a compact representation of the Legendre polynomials known as Rodrigues’ formula,

\[
P_l(\xi) = \frac{1}{2^l l!} \frac{d^l}{d\xi^l} \left[ (\xi^2 - 1)^l \right].
\]

(1.50)

The Legendre polynomials form a complete orthogonal set of functions in the interval $-1 \leq \xi \leq 1$. Thereby any function $f(\xi)$ in this interval can be expanded in terms of them:

\[
f(\xi) = \sum_{l=0}^{\infty} C_l P_l(\xi),
\]

(1.51)

where

\[
C_l = \frac{2l+1}{2} \int_{-1}^{1} f(\xi) P_l(\xi) d\xi.
\]

(1.52)
To obtain the solution of the Laplace equation (1.30) we need to provide the solution of equation (1.37), which can be written as

\[ F(r) = Ar^l + Br^{-(l+1)}. \]  

(1.53)

As a result for the problem with azimuthal symmetry \( k = 0 \) in (1.43) the solution of the Laplace equation has the form

\[ \Phi(r, \theta) = \sum_{l=0}^{\infty} \left[ A_l r^l + B_l r^{-(l+1)} \right] P_l(\cos \theta). \]  

(1.54)

1.6 **Particles small compared with light wavelength**

In this section the response of small particles with radius \( a \ll \lambda \) is investigated. To describe the response of spheres of arbitrary sizes the Mie theory should be applied [9]. However, small particles may be considered in the electrostatic approximation. In this approximation, the phase of the electromagnetic wave does not change across the particle, so the problem may be solved at the start by ignoring the time dependence of the electromagnetic wave. After finding the solution of the problem, the harmonic time dependence may be incorporated in the solution. Experience shows that electrostatic approach reasonably well describes the response of particles with the diameters up 100 nm [1].

We consider a homogeneous, isotropic sphere of radius \( a \) with a dielectric constant \( \varepsilon \) located at the origin in a uniform, static electric field \( E = E_0 z \) (Figure 1.4). The surrounding medium is considered as isotropic and non-absorbing with a dielectric constant \( \varepsilon_m \) [1, 8].

![Figure 1.4](image)

Figure 1.4. Sphere of radius \( a \) in a uniform static electric field. The field \( E_0 \) is parallel to \( z \) axes at high distances from the particle. The sphere has a dielectric function \( \varepsilon(\omega) \) and dielectric constant of surrounding medium is \( \varepsilon_m \).
Both inside and outside the sphere there are no free charges. Consequently we can find the field distribution by solving the equation (1.30) and taking into account that the electric field obeys \( \mathbf{E} = -\nabla \Phi \). As was shown above, due to the axial symmetry of the problem geometry, the general solution has the form (1.54). Since the solution should remain finite at the origin the solution for the potentials \( \Phi_{\text{in}} \) inside and \( \Phi_{\text{out}} \) outside the sphere can be written as

\[
\Phi_{\text{in}}(r, \theta) = \sum_{l=0}^{\infty} A_l r^l P_l(\cos \theta),
\]

\[
\Phi_{\text{out}}(r, \theta) = \sum_{l=0}^{\infty} \left[ B_l r^l + C_l r^{-(l+1)} \right] P_l(\cos \theta).
\]

The coefficients \( A_l, B_l \) and \( C_l \) can be determined from the boundary conditions at infinity and the radius of the sphere. From the boundary condition at infinity (\( \Phi \rightarrow -E_o z = -E_o r \cos \theta \)) we find that \( B_l = -E_o \) and \( B_l = 0 \) for \( l \neq 1 \). The other coefficients are determined from the boundary conditions at \( r = a \).

Continuity of the tangential component of the electric field \( E \) across the interface requires

\[
-\frac{1}{a} \frac{\partial \Phi_{\text{in}}}{\partial \theta} \bigg|_{r=a} = -\frac{1}{a} \frac{\partial \Phi_{\text{out}}}{\partial \theta} \bigg|_{r=a}.
\]

In the same way the requirement for continuity of the normal component of displacement field \( D \) gives

\[
-\varepsilon_0 \varepsilon_m \frac{\partial \Phi_{\text{in}}}{\partial r} \bigg|_{r=a} = -\varepsilon_0 \varepsilon_m \frac{\partial \Phi_{\text{out}}}{\partial r} \bigg|_{r=a}.
\]

Solving these equations taken together we find that \( A_l = C_l = 0 \) for \( l \neq 1 \) and for the potentials

\[
\Phi_{\text{in}} = -\frac{3 \varepsilon_m}{\varepsilon + 2 \varepsilon_m} E_o r \cos \theta,
\]

\[
\Phi_{\text{out}} = -E_o r \cos \theta + \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2 \varepsilon_m} E_o \frac{a^3}{r^2} \cos \theta.
\]

The relation for \( \Phi_{\text{out}} \) describes the superposition of the applied field and that of a dipole located at the centre of a sphere centre. Thus \( \Phi_{\text{out}} \) can be rewritten by introducing the dipole moment \( p \) as
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\[ \Phi_{\text{out}} = -E_0 r \cos \theta + \frac{p \cdot r}{4 \pi \varepsilon_0 r^3}, \quad (1.61) \]

\[ p = 4 \pi \varepsilon_0 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2 \varepsilon_m} a^3 E_0. \quad (1.62) \]

Now we can find the expression for the polarizability \( \alpha \), defined as \( p = \varepsilon_0 \varepsilon_m a^3 E_0 \)

\[ \alpha = 4 \pi a^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2 \varepsilon_m}. \quad (1.63) \]

Formula (1.63) is also known as the Clausius-Mossotti relation. It expresses the polarizability of a sub-wavelength sphere in the electrostatic approximation. At the conditions when the denominator in (1.63) is minimum, the polarizability is resonantly enhanced. Thus the dipolar localised surface plasmon resonance (LSPR) in the case of small imaginary part of the dielectric constant \( \varepsilon_i / \varepsilon_r \ll 1 \) occurs at the frequency at which the condition \( \varepsilon_r (\omega) = -2 \varepsilon_m \) is satisfied. The latter for a sphere with a dielectric function (1.18) gives the LSPR frequency

\[ \omega_0 = \frac{\omega_p}{\sqrt{2 \varepsilon_m + 1}}. \quad (1.64) \]

For a sphere located in air, the resonance of such particle occurs at the frequency \( \omega_0 = \omega_p / \sqrt{3} \).

The equation \( E = -\nabla \Phi \) applied to the relations (1.59) and (1.60) gives the following expressions for the electric field distributions

\[ E_{\text{in}} = \frac{3 \varepsilon_m}{\varepsilon + 2 \varepsilon_m} E_0, \quad (1.65) \]

\[ E_{\text{out}} = E_0 + \frac{3 n (n \cdot p) - p}{4 \pi \varepsilon_0 \varepsilon_m} \frac{1}{r^3}. \quad (1.66) \]

The resonance in \( \alpha \) leads to resonance in dipole moment \( p \), which also gives the resonance enhancement of both the internal and dipolar fields. Many applications are based on the effect of the field enhancement around the metal particles at resonant frequency: surface-enhanced Raman spectroscopy (SERS), sensing, second harmonic generation (SHG) and others. To estimate the value of the field enhancement, let us consider the depolarization field inside the particle \( E_{\text{pol}} = E_{\text{in}} - E_0 \). By using the relation (1.65) the following expression can be obtained
For metals with Drude dielectric function in the form (1.16), and in the limit of small damping $\frac{\gamma^2}{\omega^2} \ll 1$ at resonant frequency (1.64) the field enhancement may be written in the form \[10\]

$$E = E_0 \left| \frac{3i\varepsilon_m \omega_p}{(2\varepsilon_m + 1)^{3/2} \gamma} - 1 \right|. \tag{1.68}$$

For a dielectric with $\varepsilon_m \sim 1$ this gives the enhancement of the electric field of two orders of magnitude. From the relation (1.68) it is seen that the maximum level of the field enhancement is limited by plasmon damping. Significant enhancement can be obtained in the presence of the gain media when the entire denominator in (1.67) can equal zero when both real and imaginary parts vanish simultaneously \[10\]. Another way to reduce the metal intrinsic losses is the temperature reduction \[11\]. The effect of the temperature on the plasmon damping rate will be discussed in more detail in Chapter 6.

Investigation of the optical properties of nanoparticles, for example in optical microscopy, is based on measuring the absorption and scattering of incident light by nanoparticles. The quantity, which characterizes the strength of nanoparticle-light interaction in the far-field, is the cross-section. Theoretical consideration gives the following expressions for scattering and absorption cross-sections $C_{\text{sca}}$ and $C_{\text{abs}}$ \[12\]:

$$C_{\text{sca}} = \frac{k^4}{6\pi} |\alpha|^2 = \frac{8}{3} k^4 a^6 \left| \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right|^2, \tag{1.69}$$

$$C_{\text{abs}} = k \text{Im}(\alpha) = 4\pi k a^3 \text{Im} \left[ \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right]. \tag{1.70}$$

The quantity which is often measured in experiments is extinction which is a sum of scattering and absorption $C_{\text{ext}} = C_{\text{sca}} + C_{\text{abs}}$. For small particles with $a \ll \lambda$ the efficiency of absorption scales with $a^3$, while the scattering efficiency depends on $a^6$. Thus for small particles both scattering and absorption contribute to the particle extinction. For larger particles, absorption usually dominates over the scattering. Despite the fact that scattering cross-section is small, some techniques of measuring nanoparticle optical response are based
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on collecting the scattered light. One of such techniques, *dark-field microscopy*, is discussed in Chapter 2.
Chapter 2
Methods

This Chapter describes the methods of fabrication, structure characterization and experimental techniques used throughout this work. The fabrication section comprises two types of lithographic technique: standard electron-beam lithography (EBL) and nanosphere lithography (NSL). The latter technique can be extended by means of reactive-ion etching (RIE) of the arrays of polystyrene spheres in oxygen plasma. This allows the fabrication of arrays of modified NSL particles and also films perforated with nanoholes. The characterization of the fabricated structures, in addition to optical microscopy, is performed by means of scanning electron microscopy (SEM) and atomic force microscopy (AFM). The experimental techniques include the ultrafast laser measurements: pump-probe (PP) spectroscopy and THz generation and detection.

2.1 Fabrication techniques

2.1.1 Electron-beam lithography

Electron-beam lithography (EBL) together with focused ion-beam lithography (FIB) are the most common techniques for the fabrication of metallic nanostructures. They offer high flexibility in structure design [13] and future with sub-10 nm resolution [14, 15] in the case of using high resolution photoresist and optimised development process. EBL in many ways is similar to scanning electron microscopy (SEM), which operation is based on accelerating and focusing down the beam of electrons. The use of electrons is determined by their small de Broglie wavelength, which is much smaller than 1 nm for typical energy of electrons in the system. While there are several factors limiting the resolution of SEM and EBL, such as focusing the electron beam and scattering of the electrons on the resist and substrate surface, the final resolution outperforms that of the optical microscope and optical lithography, which lies in the range 300 – 1000 nm for visible light.

The typical EBL process consists of the stages schematically shown in Figure 2.1 and described below. The detailed description of the process used to prepare our structures may be found in C. Burrows’s PhD thesis [16].
Figure 2.1. Schematic of electron-beam lithography. The process comprises the following steps. The cleaned glass substrate (a) is covered by a thin layer of electron photoresist (b). The pattern is created by electron beam in the resist film (c) followed by its development (d). The final steps are metal evaporation through the mask formed in photoresist (e) and etching the structure in solvent (f).

a) **Substrate preparation.** A thorough cleaning of the substrate is required to remove all the contaminants. For this purpose we use at first cotton buds and acetone to remove large dust particles. Then the substrate is placed in turn in acetone and isopropanol and sonicated for ca. 10 min in each solvent. After each step the substrate is dried in a nitrogen stream. The acetone is used to remove the organic contaminants, whilst isopropanol cleans the substrate from any residual chemicals left from the acetone.

b) **Photoresist spin-coating** on the substrate. Depending on the thickness of the resist required different concentrations of the resist in a solvent and different rotation speeds were used. For a standard procedure the 4% solution of PMMA in anisole is used together with spinning for 90 s at 4000 rpm. This leads to the formation of a 200 nm PMMA film. Then the substrate with the resist is placed on a hot plate at 150 – 180°C for about 10 min to evaporate the remaining solvent and to smoothen the resist surface.

c) **Electron-beam exposure.** The substrate with a resist film is placed in a vacuum chamber of the EBL system and the focused electron beam is used to pattern the structure. Electrons passing through the resist modify its structure and change the solubility of the resist by altering the bonds of polymer chains. Depending on the effect caused by electron-beam exposure, resists are classified as positive or negative. In positive resists
electron exposure increases the solubility leading to dissolution of the exposed parts of the resist during the development stage. The solubility of the negative resists on the contrary is decreased by electron-beam exposure and thus only unexposed parts are dissolved during the development.

d) For development a mixture of isopropanol and pure water in the ratio 9:1 is used. The sample is placed in the mixture for one minute and slight agitation is applied. Then the sample is rinsed for one minute in pure water to remove residues of solvent.

e) Once the required structure is patterned in the resist layer, the resist mask is used to create the structure in metal. The sample is placed in an evaporator for metal deposition under high vacuum conditions. The pressure and the evaporated thickness are monitored during the process by means of the vacuum gauge and piezoelectric crystal placed in proximity to the sample. The crystal allows measurement of the deposited mass of the metal which is then converted into the thickness.

f) The last step is lift-off in a solvent. During the process the mask is dissolved leaving the required structure on the substrate. When using the PMMA as a resist, an acetone is applied for lift-off. Depending on the acetone temperature, the lift-off may take from several minutes in case of boiling acetone to several hours for cold one. Once the process is finished, the sample is rinsed in isopropanol with subsequent drying in nitrogen stream.

While EBL offers a high flexibility in pattern design allowing independent control of the size, shape and arrangements of the structures within the resolution limits, it possesses inherent limitations. Since it is a serial process, the technique is time and money consuming. This means that structures with large sizes (more than 1 mm for modern systems) are difficult to fabricate. This issue may be overcome by using parallel fabrication processes, such as optical and X-ray lithography and self-organised fabrication techniques, one of which will be discussed in the next section.

Another limiting factor is the resolution. As it was mentioned, it is not diffraction which determines the resolution of EBL. One of the main reasons limiting the resolution is electron scattering in the resist and from the substrate: forward
scattering and backscattering [17]. In addition to that, other factors limit the resolution: sensitivity of the resist, development and lift-off processes.

There are several fabrication methods which outperform EBL in resolution, such as scanning probe techniques [18]. Their operation is based on building the structure by a scanning tip, which can be used either to put the structural blocks together or by scratching the surfaces by a tip.

2.1.2 Nanosphere lithography

Self-organising fabrication techniques have the advantage over EBL and FIB in that they are parallel processes. They are fast and cheap and sometimes offer similar resolution. The payment for these advantages is a loss of flexibility. One such technique which was extensively used throughout the thesis is nanosphere lithography (NSL). It allows for facile production of large area (~ 1 cm$^2$) of ordered arrays of nanoparticles with control over the size and period of the structure. In addition, the technique may be modified to allow altering of the shape of the particles, even producing nanohole arrays.

For the first time the idea of utilising latex spheres as a self-assembled mask was used by Fischer and Zingsheim in 1981 [19] to produce a pattern for contact imaging with visible light. The technique was further developed by Deckman and Dunsmuir in 1982 [20] who showed that the mask of nanospheres may be used for material deposition. The modern stage of NSL started in 1995 after the work of Van Duyne group [21] who named the technique as it is widely referred to now. In the same group the nanosphere lithography was studied in detail and several extensions of the technique were developed [22]: double layer of the nanosphere mask, and angle metal deposition. This extended the range of structures which can be fabricated by NSL technique to isolated nanoparticles with altered shape (discs, elongated triangles), chained nanoparticles and nanorings.

As usual lithography, NSL comprises three main stages: mask preparation, material deposition and lift-off. There are several ways to transfer the nanospheres onto the substrate to produce a close-packed array, such as spin-coating or drop-casting of the solution with polystyrene spheres on the substrate surface with subsequent drying to evaporate the solvent. During this process the honeycomb structure of the spheres is produced. At the University
of Exeter we use a different technique, briefly described below. For more details see PhD theses of B. Auguié [23] and W. Murray [24].

Figure 2.2. Schematic representation of nanosphere lithography. On the left part of the figure the standard fabrication process is shown, which results in formation of honeycomb array of triangular metal nanoparticles. The right part of the figure depicts the modified NSL technique with added step of polystyrene spheres etching in oxygen plasma which reduces the spheres size and leads to the formation of nanohole structure. The inset pictures show SEM images of the sphere arrays before the metal deposition. The bottom pictures are SEM images of the final structures. The initial diameter of the spheres is 780 nm. The scale bars are 2 μm.

The substrate cleaning procedure is the same as described in previous section. The cleaned glass substrate is submerged in pure deionized water. Then a suspension of colloidal nanospheres is introduced onto the water surface. Once the spheres self-assemble in a close-packed array, the water level is lowered and a layer of the spheres is transferred onto the substrate surface. The sample is then dried out in an ambient atmosphere, normally overnight. The next step is metal deposition through the gaps between the spheres. The sample is placed in a high vacuum chamber and the metal is evaporated at pressure below $10^{-5}$ mbar at a rate of 1 Å/s. Finally, the polystyrene spheres are removed by ultrasonication in toluene to leave a honeycomb array of triangular particles.
The schematic representation of the process together with SEM images of the sphere array, and the final structure, are shown in Figure 2.2 (left).

The dimensions of the particles fabricated by NSL technique depend on the nanosphere diameter $D$. From the mask geometry the particle metrics, perpendicular bisector $h$ and side $a$ of a triangular particle, and a structure period $P$, are given by the following relations [21]

\[
h = D \left( \sqrt{3} - \frac{3}{2} \right), \quad a = \frac{2}{\sqrt{3}} h = D \left( 2 - \sqrt{3} \right), \quad P = \frac{\sqrt{3}}{2} D. \tag{2.1}
\]

The structures fabricated by using the nanospheres with diameter 780 (390) nm are supposed to have the dimensions of $h = 181.0$ (90.5) nm, $a = 209.0$ (104.5) nm and $P = 675.5$ (337.7) nm.

As mentioned above, the NSL technique may be modified to fabricate variant structures ranging from different size and shape of nanoparticles [21, 22, 25, 26] to films perforated with nanoholes [27, 28] by etching the spheres in oxygen plasma to reduce the sphere diameter. Reactive-ion etching (RIE) allows for a controllable size reduction of the polystyrene spheres and thus an alteration of the size and shape of the gaps between the spheres. This leads to a modification of the resulting structures. Three different groups of structures may be produced by this NSL technique: separated particles with slightly varying particle size and shape depending on the etching time; ordered arrays of nanoholes; and in the transition regime the combination of holes and particles. For our experiments we chose either a short etch to produce the separated particles or a longer etch for nanohole arrays fabrication (see Figure 2.2).

### 2.2 Sample characterization

#### 2.2.1 Scanning electron microscopy

*Scanning electron microscopy (SEM)* operation is based on scanning the sample surface with a focused electron beam. The interaction of the electrons with the atoms on the surface leads to different signals which can be detected to give information about the surface topography and its composition. A typical scanning electron microscope consists of an electron gun, magnetic lenses, scanning coils, and electron detectors.
The usage of electrons instead of photons is determined by their wavelength which is much shorter than the optical wavelength of the visible light. The SEM resolution, as in the case with EBL, is not limited by the diffraction of electrons, but rather by electron optics, which is not free from the lens aberrations. The best lateral resolution obtained by modern scanning electron microscopes is less than 1 nm [29].

To achieve a good resolution of electron micrograph, one should avoid charge accumulation on the sample surface. For this purpose the non-conductive surfaces have to be covered with a thin conducting layer. Normally, we use a thin layer (1 – 2 nm) of sputtered Au-Pd alloy to avoid charging artefacts.

In addition to high lateral resolution of SEM, it also has a great depth of field, which allows one to acquire the characteristic 3D image, though the vertical resolution of SEM is lower than the lateral resolution. To measure the height of an object, the sample has to be tilted and its projection on \( xy \) plane measured, which gives an estimate for the object size in the \( z \) direction. To determine the height of the object with a better accuracy, scanning probe microscopy is required. For this purpose we use an atomic force microscope, which is described in the next section.

### 2.2.2 Atomic force microscopy

**Atomic force microscopy (AFM)** belongs to the family of microscopy techniques called *scanning probe microscopy (SPM)* [30], the powerful modern techniques which are used for investigation of the solid body surfaces. All the techniques are based on the same approach of using the mediating tip to map the surface topography. The era of scanning probe microscopy started with *scanning tunnelling microscopy (STM)* invented in 1981 by Binnig and Rohrer [31, 32]. The STM operation is based on the electron tunneling effect. When the tip is brought close to the surface and the voltage between the tip and a surface is applied, the electrons could tunnel through the small vacuum gap. The tunneling current is a function of the tip position and the gap. Thus by monitoring the current, the information about the surface topography can be obtained.

The atomic force microscope was invented in 1986 by Binnig, Quate and Herber [33]. The AFM relies on measuring the force between the tip and a
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The force acting on a tip is the van der Waals force, which has a long range attraction component and a short-distance repulsion term. Thus AFM tip is attracted by the sample at large distances and repelled at short distances. By maintaining the interaction force at the same level during the surface scanning and moving the tip towards and away from the sample, one can plot the topography map of the surface.

The AFM has several advantages over the SEM. The AFM plots a truly 3D image of the surface, it does not require any special treatment of the sample and it is free of charging artefacts. The drawbacks include the small size of the scanning area and low scanning speed.

For the sample surface investigation the techniques were chosen as follows. For large scanning area and for the lateral investigation of the surface the SEM was used. The detailed investigation of the surface in vertical direction is performed by AFM.

2.2.3 Optical characterization

To characterise the optical response of the structures we primarily used two techniques: optical spectrophotometry and microspectroscopy. For the first approach the apparatus Biochrom Ultrospec 4300pro was employed. Here the white light from the lamp is passed through the monochromator and then it is directed to the sample. The intensity of the transmitted light is measured by a photodetector and compared to the reference intensity. The device features with an easy functioning, high acquisition speed and wide spectral range spanning from 190 nm to 1100 nm. Due to the large area of the illumination spot, only large structures (~ 1 cm²) could be characterised with this spectrophotometer. Another limitation of the system is that it is designed to work only in transmission mode.

In order to measure the response of small arrays of particles, or even individual particle, a microspectroscopy setup was used. It can operate in either transmission or reflection mode with two spectroscopy regimes available in each mode: bright- and dark-field. The system is based on an inverted optical microscope (Nikon Eclipse TE2000-U) combined with a spectrometer (Princeton Instruments, SpectraPro 2500i) and a charge-coupled device (CCD) camera. The structures are illuminated by white light from a tungsten-halogen lamp. The
light, after passing through the sample or reflecting from it, is collected by a proper objective. Then the light is passed through a slit situated at the spectrometer entrance to achieve a good spectral resolution. In the spectrometer the dispersed light is projected onto the 1024 × 256 lines of the CCD camera. The image from the camera is used to specify the area of interest, from which the data are collected for spectroscopy needs.

Below we briefly discuss the four used regimes of *microspectroscopy*. For more details about the data acquisition in the system used, and specifically about the *dark-field transmission* mode, see PhD thesis of C. Burrows [16].

*Transmitted bright-field (TBF) illumination.* This is the simplest of all the optical microscopy techniques. In this method only the light directly passed through the sample is collected by the objective at the other side of the sample. The image looks bright with darker areas, where the light is absorbed. The name bright-field is due to the bright background of an image and hence a good contrast can be achieved only with strongly absorbing structures. The technique is simple and gives the absolute value of the absorbance but has a drawback due to poor contrast, when the structure under study is low absorbing.

Because the lamp spectrum is not flat, the acquired signal has to be normalised spectrally using the following expression

\[
I_{TBF}(\lambda) = \frac{I_{sig}(\lambda) - I_{bg}(\lambda)}{I_{bg}(\lambda)},
\]

where \( I_{sig} \) is the light signal passed through the structure, \( I_{bg} \) is the light intensity measured from a bare substrate and \( \lambda \) is the light wavelength. Due to low contrast, the technique is rarely applied to measure the single-particle response with sub-wavelength size, as the difference between the transmitted light through the particle and bare substrate is much smaller than the signal itself. That is why the technique is mainly used to characterise the collective response of the arrays of nanoparticles. To achieve a good signal-to-noise ratio in single-particle measurements, special techniques have to be applied, such as spatial modulation with lock-in detection [34].

*Reflected bright-field (RBF) illumination.* This technique is mainly used for opaque samples and is similar to the previous technique. The main difference between the techniques is that in RBF method the same objective is used for
Both the illumination and the collection of the reflected light. For this purpose a beam splitter is used to direct the collected light into the spectrometer. In RBF technique mainly the specular reflected light is collected by the objective. The brightest parts in the image correspond to the structures with the highest reflectivity. In order to obtain a normalised signal, a reference signal has to be measured, for instance, a signal from an ideal reflector, which reflects all of the incident light at any wavelength. Metallic silver or dielectric mirrors may be used for this purpose over a wide range of wavelengths. Once the reference signal is acquired, the reflection signal from the structure may be obtained by the following expression

$$I_{RBF}(\lambda) = \frac{I_{\text{sig}}(\lambda)}{I_{\text{ref}}(\lambda)}$$  \hspace{1cm} (2.3)

where $I_{\text{sig}}$ and $I_{\text{ref}}$ are the intensities of the reflected light and reference signal respectively; $\lambda$ is a light wavelength. The technique has several drawbacks. The normalization does not take into account the reflection from the substrate which in some cases may be substantial. The intensity of the light reflected from the substrate can not be simply incorporated in the formula (2.3) as was done in (2.2) because the light reflected from the substrate passes through the structure under investigation and is absorbed by it. Thus, obtaining the absolute values of the reflected signals may be a challenge in some cases. Another limitation is poor contrast as in the case of TBF technique, which makes it difficult to measure a single particle response.

**Transmitted dark-field (TDF) illumination.** The reason for using the dark-field illumination is to obtain a high contrast image [35]. The idea which lies behind the technique is simple: in order to acquire a high contrast image, the directly transmitted or specularly reflected light has to be excluded from entering the collecting optics. For this purpose the illumination setup has a specially sized disk which blocks the middle part of the beam. The condenser illuminates the sample within the range of angles which cannot be measured by the collection objective lens, since its numerical aperture ($NA = n \sin \alpha$, $n$ is a refractive index of the media in which an objective works) is smaller then the minimum numerical aperture of the condenser (Figure 2.3). Thus only the light scattered by the structure is measured. This leads to an appearance of a dark background image with bright scattering objects. Dark-field spectroscopy is one
of the most commonly used optical techniques for single-particle investigation [36]. The high contrast of the image allows one to detect single particles and measure their scattering signals. The technique has a number of drawbacks. Some of them are general for dark-field technique, while others are specific for transmission mode. One of the issues is a normalisation procedure. To normalise the signal spectrally, the reference signal has to be measured. The easiest way is to measure the scattering intensity from a plane substrate. Here we assume that the substrate has a flat spectral scattering response. For normalisation we use the expression (2.2), where $I_{\text{sig}}$ and $I_{\text{bg}}$ are the intensities of the light scattered by the structure and by a substrate respectively. It is worth noting that dark-field signal can be normalised only spectrally and thus the values of the intensity are always arbitrary. Another limitation of the technique is a grating effect which is observed when probing periodic structures. This leads to the appearance of spurious signals due to diffraction for certain wavelengths of incident light.

![Diagram of bright- and dark-field microscopy](image)

Figure 2.3. a) The schematic of the bright- and dark-field microscopy. In the bright-field technique an objective collects only directly transmitted or specular reflected light. In dark-field technique the numerical aperture of the condenser is greater than that of the objective, so that the incident light is excluded from the measurements. Only the light scattered by the structures can be collected. In the RDF technique, the objective (b) combines two optical systems coaxially coupled, a condenser and a collecting objective.

There is also an issue with comparing the experimental data to computer model. In dark-field illumination setup the incident light has a range of k-vectors
and polarization states which are unknown. This, together with the unknown intensity distribution for the range of incident angles makes it a challenge to model the illumination setup conditions.

To compare data obtained by different techniques we measured the response in TBF, RBF and TDF illumination setups (Figure 2.4). The data are normalized to unity for the sake of comparison. The measured structures are made by EBL and consist of the rectangular shape particles with the sizes 75 by 120 nm (Figure 2.4a) and 100 by 140 nm (Figure 2.4b). The pitch size, 300 nm, and the thickness of gold layer, 40 nm, are kept constant for both arrays. The comparison shows that the resonance position and the spectral shape of the signal vary from one spectroscopy technique to another. However, though the peak wavelengths do not coincide, their values are quite close to each other, especially in the case of smaller particles. This mismatch of the resonance wavelength is somewhat expected, since even in electrostatic approximation there are different conditions for the resonance wavelength of LSPR for scattering, Eq. (1.69), and absorption, Eq. (1.70). The scattering cross-section is maximal when the absolute value of the polarizability is maximal, while the absorption cross-section is maximal when the imaginary part of the polarizability is maximal.

![Figure 2.4.](image)

*Figure 2.4. The comparison of the spectral response measured in TBF (black), RBF (red) and TDF (blue) illumination setups. The figure (a) shows the data for smaller particles with the sizes 75 by 120 nm and (b) for larger ones 100 by 140 nm. The insets depict the SEM images of the particles. The shape of the particles is slightly skewed due to an artefact of the imaging process. Each particle is rectangular in shape. The scale bar is 50 nm. The objectives used for light collection are Nikon ×150 (NA 0.90, LU Plan Apo, WD 0.42) for TBF and RBF and Nikon ×40 (NA 0.60, S Plan Fluor ELWD) for TDF.*

*Reflected dark-field (RDF) illumination.* The technique is used to improve the contrast in the reflected light microscope. It is mainly used with opaque
specimens and is similar to TDF technique. In the RDF illumination setup the condenser and an objective are combined coaxially in one optical system (Figure 2.3b). The light is sent through the outer cladding of the objective so that the illumination beam has a higher NA than the NA of the collecting objective and thus only the scattered light is collected by the objective. The technique may be used for microspectroscopy of single nanoparticles [37], the normalization procedure is similar to that of the TDF technique.

The RDF illumination has several advantages over the TDF method. Since the condenser and an objective are coupled together, their numerical apertures are adjusted to each other to achieve the best possible resolution for a combination of illuminating and collecting optics. Thus, in TDF mode the dry dark-field condensers may be used only for objectives with NA below 0.75. The objectives with higher NA require a reduction of the aperture to exclude the direct light from entering the objective. This leads to some reduction of the objective resolving power together with the decrease of the collected light intensity. The dry objectives for reflected mode may have the NA up to 0.9 with full compatibility with dark-field illumination. In addition, these objectives with high NA have a very small working distance which allows one to collect much more light than in a transmitted light setup. This solves the issue with the lack of the light intensity in dark-field illumination setup when working with high-magnification objectives.

2.3 Experimental techniques: time-resolved measurements

This section describes the time-resolved techniques used for the measurements presented in the thesis. The techniques are based on using femtosecond laser pulses which allow to investigate the temporal characteristics of the processes with temporal resolution of the order of pulse width. There are two such techniques based on ultrashort laser pulses were used: pump-probe (PP) spectroscopy and THz time-domain spectroscopy (THz-TDS).

Both setups use the same laser system, a regenerative amplifier Coherent Legend Elite. The system consists of a Ti:sapphire seed laser (Coherent Vitesse) and an amplifier. The seed laser is pumped at 532 nm and generates 85 fs pulses with an energy of 12 nJ at a repetition rate of 80 MHz with a central wavelength of 800 nm. Before amplifying, the pulses are stretched in time by a grating to avoid the damaging of the titanium-doped sapphire crystal. The cavity
Methods

is bounded by Pockels cells which control the number of passes through it. After approximately 20 round trips of the cavity the pulses are released and then recompressed to about 100 fs by a second grating. The amplified pulses have the maximum energy of 3 mJ and a repetition rate of 1050 Hz. The high pulse energies are of extreme importance for investigation of nonlinear processes.

2.3.1 Pump-probe spectroscopy

The technique is used to investigate the coherent vibrations of metal nanoparticles after illumination by femtosecond pulses. The phenomenon of the acoustic oscillations of metal particles is described in detail in Chapter 3. In brief, the instantaneous heating of electron gas by a laser pulse is followed by electron gas thermalization through electron-electron scattering and subsequent energy transfer to the lattice through electron-phonon interaction. The excitation of phonons leads to the lattice expansion which triggers its vibrations. The latter induces a periodic shift of the plasmon absorption band of a particle leading to a corresponding oscillation in the transient absorption. These oscillations are detected by measuring the change in the absorption of the probe pulse in an array of nanoparticles after illuminating them by a pump pulse. By varying the delay between the pump and probe pulses, the temporal dynamics of the oscillations can be traced.

The pump-probe setup is shown in Figure 2.5. The laser beam is split into two beams, pump and probe. The pump beam passes through frequency-doubling crystal (BBO) and a short-pass filter, to remove 800 nm light. Then the beam goes through a mechanical chopper which modulates the light at 525 Hz, half the frequency of the laser system. The delay line is used to vary the relative timing between the pump and probe pulses. The probe beam is split into two beams, one of which is used as a reference for the detection scheme and the another for probing the sample.

Initially, the pump and probe beams are spatially overlapped on the sample and colinearly aligned by means of a pinhole. The probe beam is slightly focused on the sample so as to have a uniform illumination by pump light of the structure on the size of probe beam. In order to reduce the influence of the probe beam on the system under investigation, the probe pulse intensity is chosen to be at least an order of magnitude weaker than the intensity of the pump pulse. To reduce the influence of the pump beam on the detection scheme, it is misaligned
slightly so that only the probe beam passes through the pinhole. For the same reason, long-pass filters are used at the entrances of photodiodes. The neutral density filter in the detection scheme is used to equalise the light intensities in both arms of the balanced detector in the absence of the pump pulse. The reference signal helps to reduce the noise arising from the laser system. The balanced detection and the lock-in amplifier make the detection very sensitive to small changes in the measured signal allowing one to measure the relative changes in the intensity with an accuracy of better than $10^{-5}$.

Figure 2.5. Pump-probe setup. The laser beam is divided by a splitter (Sp) into two beams, one for sample excitation (shown in blue) and the another for its probing (shown in red). The pump pulse is frequency-doubled by BBO crystal (Cr) and modulated at 525 Hz by chopper (Ch). The short-pass filter (SF) is used to remove the residual 800 nm light. The probe beam is used both for referencing the photodiodes and for probing the sample. The pinhole (P) helps to align the pump and probe beams and then to block it by a slight misalignment of pump beam. The residual 400 nm light is absorbed in the long-pass filters (LF). The neutral density filters (ND) are used to equalise the photodetectors in absence of pump beam and to reduce the probe pulse intensity. The temporal delay between the pump and probe pulses is changed by a delay line. Other optics, shown in the scheme, are mirrors (M) and lenses (L).

The typical differential transmission measurement from an array of NSL silver particles is shown in the Figure 2.6. Two regions can be clearly seen in the data, a sharp peak followed by a slower oscillation tail. The injection of energy by femtosecond laser pulse leads to heating of electron gas and then its thermalization through electron-electron and electron-phonon interactions [38]. This instantaneous thermalization causes an abrupt change in $\Delta T/T$ with
characteristic rise and fall time scales of order 100 fs and 1 ps respectively. On longer time scales the signal exhibits damped oscillations. These are due to coherent mechanical vibrations of nanoparticles which modulate metal electronic properties and thus cause a periodic shift in the absorption band of particles LSPR [39]. In order to extract the oscillations characteristic quantities, period $T$ and the damping time $\tau_0$, the oscillations can be fitted by damped cosine function,

$$S(t) = A_{0i} \exp(-t/\tau_0) \cos\left(2\pi \left(\frac{t-t_0}{T_i}\right)\right) + A \exp(-t/\tau).$$  \tag{2.4}$$

The index $i$ designates number of cosine functions used in the fitting procedure. The expression (2.4), applied to the data in Figure 2.6, leads to a good fitting of experimental data and gives the period of oscillations $87.30 \pm 0.05$ ps and damping time of $303 \pm 4$ ps.

![Figure 2.6](image)

Figure 2.6. Differential transmission measurements on an array of NSL silver nanoparticles made by spheres with diameter of 780 nm, the particles height is 70 nm. The insets show the zoomed regions of the initial sharp peak (left panel) and of the subsequent oscillations (right panel). The experimental data are shown in black, while the fitted data are shown in red. Single frequency oscillation fitting gives the value for a period of oscillations of 87.3 ps.

From the dimensional analysis one would expect the period of vibration of the spherical particle to have the form of $T = \frac{2d}{c_l}$, where $d$ is a diameter of the particle and $c_l$ is longitudinal speed of sound in the bulk material. An exact consideration of the problem gives an expression that differs from the one...
shown above only by a dimensionless parameter [40] (for more details see Chapter 3). This relation can be also applied for an approximate calculation of the period for non-spherical particles, triangles in our case [41]. The speed of sound in the silver is 3650 m/s so the period 87.3 ps corresponds to the size 160 nm which is in rather good agreement with the size of perpendicular bisector of triangular nanoparticles in the experiment, ~180 nm, taking into account the approximate formula for the period of oscillations.

2.3.2 THz time-domain spectroscopy

This section describes the standard THz-TDS setup. The generation and detection of THz frequency radiation in the spectrometer is based on nonlinear processes: optical rectification (OR) of femtosecond laser pulses and femtosecond electro-optic sampling (EOS).

Figure 2.7. Schematic of the collimated THz time-domain spectrometer. The laser beam is split into two beams, one for generation of THz radiation and another for its detection. The radiation is generated in the sample and detected by ZnTe crystal through electro-optic effect. Due to applied THz field in ZnTe crystal the initially linearly polarized pump pulse becomes elliptically polarized. This change of the polarization state is measured by means of splitting polarizer and pair of photodiodes. The quarter-wave plate is used to balance the detector in absence of THz radiation. The delay line is used to scan temporarily the broad THz pulse (~ 1 ps) by a short probe pulse (~ 100 fs).
Optical rectification [42] is a nonlinear process of difference frequency mixing and results in the generation of DC or low-frequency polarization in media with a second order nonlinearity. For a femtosecond laser pulse, owing to its large spectral bandwidth, difference frequency mixing results in electromagnetic waves in the terahertz region. Electro-optic sampling [43] is based on a linear electro-optic effect, which describes the change in optical properties of a crystal due to an applied electric field. EOS allows an instantaneous recording of the strength of the generated field and thus the generated pulse can be traced in the time-domain.

In the standard THz spectrometer there are two nonlinear crystals, one for the generation of THz radiation and another one for detection. In the setup employed in our experiments the generation crystal is replaced by the sample under investigation. For detection we use zinc-telluride (ZnTe), a widely used nonlinear crystal for THz applications [44].

The spectrometer is shown in Figure 2.7. The pulses from the Coherent Legend laser system were split into two beams, one for THz generation and another for detection of the emitted THz radiation. The THz pulses produced by the sample were first collimated and then focused on ZnTe crystal. Since THz pulses are significantly longer than the laser pulses (several ps compared to 100 fs), the THz field can be approximated as a static field biasing the detection crystal. The THz field induces birefringence in the crystal, and this induced birefringence modifies the polarization state of the 800 nm detection pulse that is coincident with the THz pulse on the crystal. The change in polarization state is measured using a polarizing beam splitter and a pair of balanced photodiodes. A quarter-wave plate placed before the polarizer is used to ensure the polarization states are balanced when no THz field is present. For sufficiently small modulations of the polarization plane angle, the intensity change in the detector is linear with the applied THz field strength. By varying the delay between THz and probe pulses the temporal profile of the detected THz field can be obtained. The spectrum of the generated THz radiation is obtained by performing a Fourier transform of the time-domain signal. Typical time- and frequency-domain signals from a ZnTe crystal are shown in Figure 2.8.

Since THz radiation is absorbed in air due to the presence of water vapours, the generated radiation is partially absorbed in the spectrometer. This absorption
manifests itself in the appearance of dips in the measured spectra corresponding to water absorption lines and additional oscillations in time-domain signal after a short single THz peak. To obtain a real spectrum of the emitted radiation or for spectroscopy needs it is necessary to dry the air inside the spectrometer. For that reason the part of the spectrometer shown in Figure 2.7 enclosed in dashed line rectangle is put in a partially sealed box. During the data collection the box is constantly ventilated by air passed through a Du-Cal Drierite desiccant which creates a low humidity environment inside the spectrometer.

Figure 2.8. Typical trace of the time-domain signal from a ZnTe crystal measured in THz spectrometer (a). The spectrum of THz pulse (b) is obtained by Fourier transform of the time-domain signal.
Chapter 3
Acoustic oscillations

In this Chapter we report on the investigation of the coherent acoustic vibrations in nanoparticles. The acoustic phonon modes in nanostructures can be excited by ultrafast laser pulses which are, at the same time, used for monitoring the vibrational modes. The employed technique, ultrafast transient absorption spectroscopy, have been extensively used in the last two decades to study the phonon vibrational modes in nanometer sized objects with high precision and for the investigation of the elastic properties of materials on the nanometer scale, as well as mechanisms of energy exchange between nanoparticles and the environment [45].

This Chapter is organised as follows. In the first two sections we outline the theoretical background of the processes occurring in metallic nanoparticles after femtosecond laser pulse excitation. In the first section the response of electrons in a metal and their interaction with a phonon system after excitation is described. The second section deals with phonon vibrational modes in nanoparticles. In the third section we report our experimental results on the topic. We have investigated how the vibrational particle response depends on the pump intensity, particle morphology and its environment. Some of the experiments, such as the dependence of the oscillation period on the particle thickness and also on the pump intensity, have been previously reported in the literature, and here we repeat them with slight changes in the experimental parameters. Other measurements, the dependence of the vibrational particle response on the particle shape and the thickness of the metal overlayers, have been performed, to the best of our knowledge, for the first time.

3.1 Two-temperature model

The response of metal nanoparticles to ultrafast laser excitations occurs in several steps. Once the laser pulse is absorbed, the electrons gain energy which is then rapidly redistributed over the entire electronic system. This creates a hot electron population [46, 47]. On a time scale of few hundred femtoseconds the energy is redistributed between all the conduction electrons through electron-electron (e-e) scattering. Due to process of electron
thermalization the electron subsystem as a whole acquires a new temperature $T_E$. The hot electron distribution subsequently relaxes by electron-phonon interactions (e-ph) leading to an energy exchange between the electron and phonon subsystems on a picosecond time scale [48]. The energy gained by the phonon system leads to a lattice temperature increase and causes a lattice expansion. This process launches the coherent vibrational modes of the particles which subsequently decay in time due to energy exchange between the phonon system and environment.

Figure 3.1. Schematic of the energy distribution and their temporal characteristics in noble metals after laser excitation.

The processes of heat exchange between electrons and phonons are often described by the two-temperature model (TTM). The electron and phonon subsystems are characterized by their transient temperatures $T_E$ and $T_L$ and they exchange energy in a way that depends on the temperature difference, described by the coupled rate equations [38, 49]:

$$
C_E(T_E) \frac{\partial T_E}{\partial t} = -G(T_E - T_L),
$$

$$
C_L \frac{\partial T_L}{\partial t} = G(T_E - T_L).
$$

(3.1)
In these equations $C_E$ and $C_L$ are the electrons and phonons heat capacities respectively; $G$ is the electron-phonon (e-ph) coupling constant [50]. The heat capacities are temperature-dependent and thus the equations are non-linear. The heat capacity of Fermi-Dirac distributed electrons has a simple form $C_E(T_E) = \gamma T_E$, where $\gamma$ is a constant.

Since the lattice heat capacity is over two orders of magnitude larger than the electronic heat capacity [51], the maximum change of the lattice temperature is much smaller than the initial electronic temperature. In the low-excitation regime for which the temperature change $\Delta T_E = T_E(0) - T_L << T_L$ the electronic temperature decays nearly exponentially with the time constant $\tau = \gamma T_E(0)/G$ [52, 53]. In the opposite regime of high pump intensities the temperature dependence of the lattice heat capacity has to be taken into account, this leads to a non-exponential decay of the electronic temperature.

The last step in electron-phonon thermalization is heat diffusion into the environment and in the reverse direction [54]. This process occurs on a 100 ps time scale and leads to decay of the nanostructure vibrations which are discussed below in detail.

### 3.2 Acoustic oscillations

The energy deposited by a laser pulse into a metal particle causes lattice heating and thus particle expansion. Since the phonon thermalization process is much faster than the period of particle vibrations (for particles with diameter bigger than 20 nm [39]), the acoustic oscillations are excited coherently. The sudden particle expansion launches the vibrations of the particle which lead to periodic expansion and contraction of the particle. The change of the particle volume causes a change of the electron density and thus, according to the relations (1.17) and (1.64), leads to a shift in the plasmon resonance position. By measuring the transient absorption at a fixed wavelength in an array of identical nanoparticles the oscillations in the signal can be monitored. The transmission signal is modulated at the same frequency as the coherent lattice vibrations. The phenomenon was investigated on samples fabricated by the NSL technique. For the details of sample fabrication and experimental setup see Chapter 2.
The shape of the vibrational modes and their eigenfrequencies could be found from the continuum mechanics calculations. An analytical solution for the vibrational modes in spherical particles was developed by Lamb in 1882 [40]. The theory predicts two types of vibrations: spheroidal and torsional modes [55]. The vibrations of the first type occur along the radial direction, and the torsional modes have the lattice displacement in the directions along and perpendicular to the sphere radius. The torsional vibrations feature no particle volume change and thus they do not change the transient absorption band. These oscillations could not be detected by optical methods. In contrast, spheroidal (breathing) modes are characterized by change of the particles volume. Oscillations of this type can be investigated by transient spectroscopy. The lowest fundamental breathing mode excited in a sphere has a period $T_{br}$ defined by a relation [40]

$$T_{br} = \frac{2\pi R}{\eta c_i}.$$  \hspace{1cm} (3.2)

Here $R$ is the particle radius, $c_i$ is the longitudinal speed of sound in the metal, and $\eta$ is an eigenvalue which could be found as a root of the equation

$$\eta \cot \eta = 1 - \frac{\eta^2}{4\delta^2},$$ \hspace{1cm} (3.3)

where $\delta = c_l/c_i$ is the ratio of transversal and longitudinal speeds of sound. For gold with transverse and longitudinal speeds of sound equals 1200 and 3240 m/s, respectively, the eigenvalue $\eta$ from the equation (3.3) is calculated to be 2.93 [56].

In this study the acoustic oscillations of prismatic particles are investigated. Whilst there is no analytical expression for the vibrational modes of such particles, experiments show that the period of oscillation for the lowest mode can be found from the expression [41]

$$T_{tr} = \frac{2h}{c_i},$$ \hspace{1cm} (3.4)

where $h$ – is a perpendicular bisector of triangular nanoparticle.

It is interesting to note that there is an additional mechanism that makes a substantial contribution to launching lattice vibrations in small particles. In large particles ($R > 10$ nm) the main role in particle expansion plays the lattice heating contribution. In small particles the pressure from hot electron gas
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induces an extra kick for lattice expansion [39]. These two contributions could be distinguished by different phases of oscillations [57]. This is because the impact from the hot electron gas is only important at the initial moments before cooling down of the electron subsystem through the electron-phonon interaction. Thus the force from the hot electrons acts during a short period of time and rapidly decays; it can be represented as a delta-function like perturbation. The expansion from the lattice heating decays slowly on time scale of energy transfer from the particle to environment. Thus the time dependence of this contribution is given by a step-like function. The force from hot electrons is important for small particles since their period of oscillation is comparable to the electron-phonon interaction time and thus the contribution increases with decreasing particle size. Since our experiments are conducted with particles of about 200 nm in size, the role of electron pressure on lattice vibrations is negligible.

After a short time (~ 1 ps) of lattice heating through energy transfer from hot electrons to phonons, the particle oscillates between the contracted and expanded states with its equilibrium position corresponding to a size of particle with the new lattice temperature. The contraction and expansion of the particle during the oscillations causes the change of plasmon band and thus the amplitude and phase of the oscillations in the transient optical transmission signal strongly depend on the probe wavelength.

In the experimental setup (see Chapter 2) the measured signal is the difference in transmission between non-perturbed particles and ones excited by the pump pulse. The shift in plasmon resonance position may be estimated from a simple consideration of the LSPR resonance wavelength dependence on the free electron density $n$ (formulae (1.17) and (1.64)). In this model it is assumed that the dielectric function is described by the approach of free electrons. For spherical particles in a homogeneous environment the LSPR maximum is proportional to $n^{1/2}$. From the known change in the particle size the shift in plasmon resonance wavelength can be calculated. The typical relative size change of spherical particles during the oscillations is less than 1% [58]. This gives the resonance maximum shift of the order of several nanometers which is much smaller than the width of the respective plasmon resonance. Due to the change in free electron density the damping of the plasmon resonance also
changes [58]. For the sake of simplicity, and due to low perturbation in the particle size, we assume no change in the shape of the LSPR. In this approach the differential transmission signal in the limit of small perturbation can be written as

$$\Delta A(\lambda,t) = A(\lambda,0) - A(\lambda,t) \approx \frac{\partial A(\lambda,t)}{\partial \lambda} \Delta \lambda.$$  \hspace{1cm} (3.5)

From this expression it follows that the maximum signal can be obtained at the wavelength where the transmission spectrum has the steepest slope. Another interesting consequence of the formula is that the minimum in the amplitude of the signal modulation occurs at the plasmon resonance wavelength, since the absorption derivative is zero at this wavelength. Experiments show that the differential absorption signal indeed strongly depends on the probe wavelength and is nearly vanishing at the wavelength of unperturbed plasmon resonance. As expected, the phase of the oscillation undergoes an inversion at this point [41, 58].

### 3.3 Experimental results

To investigate the phenomenon of phonon oscillations in nanoparticles and their dependence of the vibrational modes on the particles size and shape we carried out transient optical transmission measurements on several sets of samples consisting of arrays of NSL particles and nanoholes. Firstly, by adjusting the pump intensity we investigated how the particles’ response varies with the intensity of the pump pulses. Secondly, the dependence of the period of acoustic oscillations on the particles’ thickness was investigated. Thirdly, the effect of particle shape is studied. For the last experiments the samples were produced by modified NSL technique causing an alteration of the particles’ shape and size and leading to continuous transformation of the nanoparticles to nanoholes. In addition, the transient transmission response from metal films perforated with nanoholes is measured. The fourth section deals with symmetry of the particle shape and its importance to the vibrational modes of the particles. Finally, the sensitivity of particle acoustic oscillations to the environment is investigated.
3.3.1 Intensity dependence

In the analysis of acoustic oscillations described in the literature and in the modelling of lattice vibrations \([59, 60]\) it is assumed that the relative amplitude of vibrations is small. Indeed, the typical value of the laser induced change of particles size is of order of 1% \([41, 58]\). Such small deformations should lead to a linear response of the particles. It is clear that higher excitation energies should cause stronger vibrational amplitude, where the linear mechanical approach may no longer be applicable. To investigate the particles response in the linear regime low pump intensities should be used. However, low pump energies cause small changes in the transmission signal, which makes it difficult to acquire the signal with a good signal-to-noise ration. To adjust the pump intensity to the level where the particles response is still linear and the signal-to-noise ratio is high enough, we measured the differential transmission signal at different pump intensities and investigated how the particle response scales with incident intensity. The experiments are carried out with NSL particles made by spheres 780 nm in diameter and 100 nm thick of deposited silver. The incident intensity is varied in the range from ca. 5 to 50 GW/cm\(^2\). The results are shown in Figure 3.2. To find out how the signal scales with incident intensity we plot the amplitudes of the first and the second positive peaks, the data are shown in the inset of Figure 3.2a. The first (high) bleach peak is due to the electron response of the metal, while the height of the second peak depends on the amplitude of particle vibrations. It is interesting to note, that the amplitude of the first peak scales nearly linearly in the whole range of applied incident intensities in accordance with previously reported data \([61]\) for the range of pump intensities below 25 GW/cm\(^2\), while the second peak scales linearly only up to the intensity of 30 GW/cm\(^2\), then the signal saturates. In addition, the shape of the first peak does not show any change (see top inset in Figure 3.2b), while the oscillation signal undergoes shape alteration at high pump intensities (see bottom inset in Figure 3.2b). It is likely that high pulse energies also cause irreversible changes in the particles shape.

To extract the parameters of the oscillations we fitted the experimental data with a double-frequency function of the form (2.4). The results indicate that for intensities below 30 GW/cm\(^2\) there are nearly no changes in the periods of both oscillations, giving the values of 88.13 ± 0.02 ps and 68.2 ± 0.5 ps for the first
and second vibrational mode, respectively, with the spread of the mean values across the measurements stated after the plus-minus sign.

These results show that the amplitudes of electron response of metal and lattice vibrations at small incident intensity depend linearly on pump power. In addition, they indicate the maximum intensity of pump pulses at which the oscillation signal is still linearly scaling with incident intensity. This means that for investigation of acoustic oscillations pump intensities below ca. 30GW/cm² should be applied.

Figure 3.2. The panel (a) shows differential transmission signal from NSL particles fabricated with 780 nm diameter nanosphere mask and 100 nm thick silver layer. The intensities used in the experiment are 5.8 GW/cm² (blue), 18.4 GW/cm² (dark green), 29.1 GW/cm² (red) and 53.0 GW/cm² (black). In the inset of (a) the amplitude of the first and the second peaks as a function of incident intensity is plotted. The amplitude (black dots) linearly depends on pump intensity (solid line is a linear fit to the data); the amplitude of the second positive peak (red triangles) shows saturation at intensity higher than 30 GW/cm². Enlarged oscillation signal is shown in (b) with insets depicting zoomed first peaks (top inset) and normalized oscillation signal (bottom inset).

3.3.2 Thickness dependence

The acoustic oscillations of prismatic nanoparticles were investigated for both chemically grown particles [60] and those made by NSL technique [41] and the periods of oscillation are measured as a function of particles size. For gold and silver particles the measured vibration periods were compared to those predicted by an empirical relation (3.4). It was found that in accordance with the theoretical prediction the period of oscillations depends linearly on the particle size. Moreover, for silver triangular particles even the prefactor of 2 in the formula (3.4) was found to match the experiment [62]. However, in case of gold particles a small deviation is observed.
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The linear dependence of the period of oscillation of prismatic particles with lateral size confirms the assumption that the particles vibrate in the plane of substrate [62]. Furthermore, the modelling of the particle vibrations by solving the elastodynamic problem gives the solutions for in-plane vibrational modes with the periods of oscillation equal to those measured experimentally for the modelled structures [60]. To gain more insight into the nature of acoustic oscillations in triangular-shaped particles and to investigate how the period of oscillation depends on the aspect ratio of these particles, we carried out measurements on arrays of NSL nanoparticles made by polystyrene spheres with a diameter of 780 nm and different thicknesses of evaporated metal. The details of the fabrication and experimental techniques are described in Chapter 2.

![Figure 3.3](image)

Figure 3.3. a) Extinction spectra of arrays of NSL silver particles fabricated with polystyrene spheres of the diameter 780 nm. The particle heights are 30, 50, 70 and 100 nm. The spectra are acquired by a microscope spectrometer in the TBF mode. b) Transient transmission measurements on these structures. The colours of the curves correspond to those in figure (a), namely, red for 30 nm, dark yellow for 50 nm, green for 70 nm and blue for 100 nm. The black dotted lines are fits of the experimental data by the relation (2.4). Single frequency fitting is used for particles with thicknesses 30 – 70 nm and double frequency fitting for 100 nm. The extracted periods of oscillations for particles 30 – 70 nm are plotted versus particle heights in the inset.

The experimental results are shown in Figure 3.3. Extinction spectra of the samples are acquired by microspectroscopy. As expected, the plasmon resonance wavelength shifts to the blue side of the spectrum with increasing the particle height [63]. Due to resonance shift, the relative position of the probe wavelength (~ 800 nm) to the resonance maximum changes with varying the thickness of particles. However, it was shown that the period of oscillations in homogeneous samples is not sensitive to the exact position of the probe
wavelength [59, 60]. Thus the measured periods of oscillation for particles with
different heights could be directly compared with each other.

To extract the period of oscillation and the decay constant, we fit the
experimental data by the relation (2.4). The measured differential transmission
signals are shown in Figure 3.3b. It can be easily seen that the oscillation period
is not changed strongly for the particles with different heights in accordance with
previously published results [41], [59]. Indeed, the extracted periods for particles
with thicknesses 30 – 70 nm vary from 85.3 ps to 90.3 ps, giving only about 6%
of change in the oscillation period for particles which differ in height more than
two times. This confirms the assumption that the observed particle oscillations
are in-plane breathing lattice vibrations. For particles with high aspect ratio
(height of the particles to its lateral size) the transient transmission signal
becomes more complex. In particular, the data for particles with thickness 100
nm shows multiple frequency response. This probably means that in particles
with high aspect ratio additional breathing mode are excited [59], [64]. In the
reports [59, 60] the vibrational eigenmodes have been calculated The lowest
frequency mode is associated with movement of the particle tips with small
displacement of the edges. For the second mode the edges are mostly moving
while the tips are nearly stationary. It was also shown [59] that the linear
dependence of the period of oscillation on the lateral size does not hold for
particles with high aspect ratio. However, for particles with a low aspect ratio the
approximate relation (3.4) gives a good estimation for the vibrational period.

The slight dependence of the period of oscillation on the particle thickness can
be also explained by small changes in the in-plane particle size due to
scattering of silver atoms during the metal deposition process. In addition, due
to fabrication geometry the shape of particles slightly changes with increasing
the height, particles become truncated tetrahedral in shape. Similar results were
obtained for silver and gold prismatic particles made by NSL technique [62],
[64]. It was reported about several percent of change in the period of
oscillations for silver and gold particles with thicknesses 30 and 50 nm and
lateral size around 100 nm [62].

The vibrational periods for particles in our experiments are shown in the inset of
Figure 3.3b where they are plotted versus the particles height. The extracted
period follows the linear law for the thicknesses of deposited silver 30 – 70 nm.
Acoustic oscillations

To fit better a more complex signal from 100 nm particles we used a relation (2.4) with two frequencies. The extracted parameters of the fitting are given in the Table 1.

<table>
<thead>
<tr>
<th>Thickness, nm</th>
<th>$A_0$</th>
<th>$\tau_0$, ps</th>
<th>$\tau_\sigma$, ps</th>
<th>$T$, ps</th>
<th>$\tau$, ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>9.63 ± 0.31</td>
<td>107.1 ± 4</td>
<td>57.8 ± 0.2</td>
<td>85.3 ± 0.4</td>
<td>-2.8 ± 0.1</td>
</tr>
<tr>
<td>50</td>
<td>18.17 ± 0.08</td>
<td>148.2 ± 0.8</td>
<td>69.1 ± 0.03</td>
<td>88.1 ± 0.04</td>
<td>-11.7 ± 0.03</td>
</tr>
<tr>
<td>70</td>
<td>4.67 ± 0.15</td>
<td>367 ± 23</td>
<td>66.1 ± 0.3</td>
<td>90.3 ± 0.2</td>
<td>15.1 ± 0.1</td>
</tr>
<tr>
<td>100</td>
<td>7.06 ± 0.09</td>
<td>189.8 ± 2.7</td>
<td>66.65 ± 0.12</td>
<td>87.7 ± 0.1</td>
<td>5.42 ± 0.02</td>
</tr>
</tbody>
</table>

Table 1. Extracted parameters of the particles lattice oscillations made by NSL technique with sphere diameter 780 nm and different thickness of silver evaporated. The expression (2.4) is used to fit the experimental data.

One can also notice from the data in Figure 3.3b that the oscillations for smaller particles, 30 nm in height, decay faster than those for bigger particles. Qualitatively, this can be understood by taking into account that the speed of heat transfer from the particle to the surrounding media is proportional to the surface area of the particle, while the stored energy is proportional to its volume. Thus, the damping time depends on the ratio of particle surface area to its volume. For thinner particles this ratio is smaller and thus the damping is faster. A careful investigation of energy dissipation from spherical particles in aqueous solution to the environment shows that the heat transfer indeed depends on the particle size [65]. Moreover, it was shown that in accordance with theoretical prediction the relaxation rate for particles with sizes ranging from 4 to 50 nm is proportional to the square of the particle radius. For particles in our experiment the damping time also shows a monotonic increase for particles with thicknesses 30 – 70 nm, as expected from this qualitative description.
3.3.3 Particle shape

To investigate how the shape of a particle affects the period of its lattice vibrations, we prepared a set of samples by modified NSL technique (see Chapter 2) and carried out transient transmission measurements on them. The masks for metal deposition are fabricated by spheres with diameter 780 nm. In order to reduce the sphere diameter, we etched the prepared mask in an oxygen atmosphere. This allowed us to continuously reduce the sphere diameter down to 660 nm, obtained for the longest etching time used during the fabrication. The thickness of deposited silver is 50 nm for all samples in the set.

As it was mentioned in Chapter 2, three different types of structures can be obtained by varying the etching time (ET). For conditions of our fabrication process, the ET below 90 s results in the particles with elongated tails as shown in Figure 3.4. The ET longer than 210 s results in fabrication of nanohole arrays. In the middle range of ET the mixture of connected and separated particles is obtained.

![Figure 3.4. SEM images of nanoparticles fabricated by modified NSL technique. The sphere diameter before etching is 780 nm. The images correspond to different etching time, 0 (unetched), 40 and 80 s, from the left to the right, respectively. The average sphere diameter reduction is 10 nm for 40 s. The images are taken at a voltage of 5 kV and electron current 0.40 nA; the magnification is 150000. The scale bars are 500 nm. For imaging purposes the samples are fabricated on ITO substrates, while the experiments are conducted with samples made on glass substrate. The presence of ITO does not affect the shape and size of the particles.](image)

In accordance with the structure geometry, the results of transient absorption measurements could be divided into three groups. The response from the samples with ET below 90 s shows the single frequency oscillations with a period of unetched sample. For ET longer than 210 s no oscillations were detected, which probably means that there were no strongly excited breathing modes. In the middle range of ET, from 90 s to 210 s, the oscillations were
Acoustic oscillations detected, though their character is much more complex than in the case of separated particles. To fit the data corresponding to ET between 90 s and 210 s, double frequency fitting is used.

The extracted parameters of the fitting are given in Table 2. The surprising result is that the oscillations for particles with ET up to 60 s have the same period as unetched particles. This is despite the fact that the particle size is changed significantly. Thus, the size of the perpendicular bisectors for the particles are 190 ± 10 nm for unetched structures, 230 ± 10 nm for particles after 40 s etch and 250 ± 10 nm for 80 s etch (see Figure 3.4), giving a change of the lateral size of about 30% without detectable change of the period of lattice vibrations. To explain these results the full elastic modelling is required. However, qualitatively, the results mean that the inhomogeneous change of the particles shape in the way as it is done in the experiment does not introduce significant change in the period of oscillations. Most probably, this is because the long and thin particle tails do not play a significant role in the lattice breathing modes.

<table>
<thead>
<tr>
<th>Etching time, s</th>
<th>$A_0$, ps</th>
<th>$\tau_0$, ps</th>
<th>$\tau_c$, ps</th>
<th>$T$, ps</th>
<th>$A$</th>
<th>$\tau$, ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.72 ± 0.03</td>
<td>321.5 ± 5.2</td>
<td>33.58 ± 0.12</td>
<td>91.41 ± 0.06</td>
<td>21.27 ± 0.02</td>
<td>868.5 ± 2.8</td>
</tr>
<tr>
<td>30</td>
<td>5.80 ± 0.05</td>
<td>276.6 ± 3.4</td>
<td>29.54 ± 0.09</td>
<td>91.62 ± 0.06</td>
<td>11.74 ± 0.03</td>
<td>566.8 ± 3.0</td>
</tr>
<tr>
<td>60</td>
<td>4.77 ± 0.03</td>
<td>228.8 ± 2.3</td>
<td>35.84 ± 0.09</td>
<td>90.84 ± 0.06</td>
<td>6.74 ± 0.02</td>
<td>334.3 ± 1.8</td>
</tr>
</tbody>
</table>

Table 2. Extracted parameters of the lattice vibrations for particles made by modified NSL technique with spheres 780 nm and different etching time. The thickness of the deposited silver is 50 nm for all the structures.

Another interesting observation can be made from the data in Table 2. The decay time $\tau_0$ of the oscillations is reduced with an increase in the etching time. This can be explained by the fact that the number of connected particles increases with increasing of the particle size, together with a reduction of the homogeneity of the sample. We note that the relaxation time depends not only on the energy dissipation rate but also on the level of interparticle correlation of the phases and frequencies of oscillations. For the same reason different
relaxation times were reported for a single pair of particles and for an ensemble [59].

For ET between 90 s and 210 s the fabricated structures consist of both separated particles and connected ones. This leads to the signal becoming more complex. To fit it at least two frequencies are required, which reflects the fact that some particles become connected. For ET longer than 210 s the transient transmission signal does not show any pronounced oscillation character, which means that most of the separated clusters are now connected. This also indicates that the continuous silver layer perforated with nanoholes does not support any detectable vibrations. In addition, the experiments carried out with a continuous silver film of the same thickness, 50 nm, also show no pronounced acoustic oscillations. To corroborate that the transition between disconnected and connected arrays occurs for ET around 200 s, we measured the resistivity of the structures (inset of Figure 3.5b). It is clear that the resistivity drops for ET longer than 200 s.

![Figure 3.5](image)

**Figure 3.5.** Differential transmission measurements on arrays of modified NSL structures. The diameter of spheres in lithographic mask is changed by etching spheres in oxygen environment. Etching time is shown in figures in seconds. The 0 s corresponds to unetched sample. The initial sphere diameter was 780 nm, the thickness of evaporated silver is 50 nm for all structures. Etching time shorter than 90 s (a) leads to formation of separated particles with changed geometry; etching from 90 s to 210 s (b) causes the connection between the particles; longer etching time leads to fabrication arrays of nanoholes. The dotted lines are the fits to the experimental data. Single frequency fitting is used for the data in (a) and double frequency for the data in (b). The inset in (b) shows the dependence of the structures resistivity as a function of ET.

### 3.3.4 Asymmetrical NSL particles

The acoustic oscillations investigated so far are described for symmetrical particles. However, in reality the fabricated structures have defects which break
Acoustic oscillations

the symmetry. The mechanical models used to simulate the vibrational modes [59, 60] assume the perfect shape of the particles. To investigate how the symmetry of the particles affects the vibrational modes, we manufactured a set of NSL particles with distorted shape and carried out the transient transmission measurements. The particles were fabricated by angle-resolved nanosphere lithography (AR NSL), a technique of fabricating NSL particles with altered shape and interparticle distance by depositing a metal at an angle to the normal [25]. The angle-resolved evaporation alters the particle shape and breaks its symmetry. The level of the shape distortion can be adjusted by varying the angle of evaporation. For these experiments we fabricated a set of 4 samples formed from spheres with diameter 780 nm and by depositing 100 nm layer of silver at angle from 0 to 30 degrees. The transient transmission data are shown in Figure 3.6.

![Figure 3.6. Transient transmission signal for arrays of NSL particles fabricated by AR NSL technique. The angle of evaporation is shown in the picture. The data for undistorted particles marked as “0 deg” is shown as a reference. The curves are upshifted for the sake of comparison. The black dotted lines show the fits to experimental data.](image)

It is visible from the data that in deformed particles the acoustic oscillations decay faster, and for strongly distorted particles extra vibrational modes appear. Due to the strong decay in the oscillation amplitude of the signal from the deformed particles, the extraction of the oscillation parameters presents a challenge. Since the single-frequency function can adequately fit only the data
for particles evaporated at angle 0 and 5 degrees to the normal, the comparison was made only for these two cases. While the period of oscillation changes by a small amount, from 88 ps for symmetric particles to about 80 ps for asymmetric ones, the change in decay time is significantly stronger, from 220 ps for undistorted particles to about 50 ps for deformed ones. Increasing the angle of evaporation to 10 degrees leads to an even stronger decay of the signal. The single-frequency function could no longer be satisfactorily fit to the signal from these particles, as it is seen from Figure 3.6. The further increase of the evaporation angle to 30 degrees gives rise to more pronounced oscillations of more complex character. This indicates that extra vibrational modes are excited in strongly distorted particles.

Strikingly, a small distortion of the particle shape introduces so strong modification of the signal. This means that the particle symmetry plays a crucial role for excitation of lattice vibrations, and in real systems the large variation of the parameters of the signal oscillation from particle to particle could be observed. This can explain the large variation of the decay time in measurements on single pair of particles [59].

3.3.5 Surrounding medium

There are many studies of the influence of the surrounding medium on the decay time of particle vibrations. The damping of the acoustic phonon modes are investigated both in the ensemble experiments [54, 66, 67] and single particle studies [61, 68, 69]. To investigate the damping of the particle oscillations, the effects of intrinsic damping should be separated from that of the environment. This can be done, for example, by measuring the vibrational response of the particles over a trench and comparing it with that on a substrate in an air or water environment [70].

It was shown that the environment of the particles plays a critical role in energy relaxation of acoustic vibrations [59, 71]. In our study we also investigate the effect of the surrounding medium on particle acoustic oscillations. This is done in two ways: by changing the type of substrate from glass to ITO-coated glass and by depositing a thin metal layer on top of particle array.

For the first set of experiments two types of samples were used, consisting of NSL particle arrays fabricated on glass and ITO-coated glass substrates. The
metal particles are fabricated by depositing 50 nm of silver through the mask of polystyrene spheres with diameter 780 nm. The differential transmission signals from both structures are shown in Figure 3.7. The solid lines depict the experimental data, while the dotted lines are fits. The signal from the glass substrate sample shows a single-frequency response with an oscillation period of 88 ps and decay time of 150 ps. The oscillation signal from the ITO substrate sample is more complex and requires at least two-frequency function. The fitting gives the following values: periods of oscillation 78 and 52 ps and decay times 66 and 295 ps. From the fitting and also from the Figure 3.7 it is clear that the vibrational mode changes: the period of oscillation and the decay time are shortened.

Figure 3.7. (a) Transient transmission measurements on arrays of NSL particles fabricated from polystyrene spheres with diameter of 780 nm. The thickness of deposited silver is 50 nm. The solid lines show the signal from arrays of particles on glass (black) and ITO-coated (red) substrates. The dotted lines are fits to the experimental data. The data from the sample made on glass substrate are fit with single-frequency function, while fitting the data from the sample made on ITO substrate require at least two-frequency function. For ease of comparison, the signal from ITO sample is multiplied by factor 4.4, and the signal from glass substrate sample is shifted down. (b) SEM micrograph of ITO-coated substrate. The scale bar is 500 nm.

One can attempt to explain these results by the grainy structure of the ITO layer (Figure 3.7b), which can affect the quality of the fabricated particles reducing their reproducibility and increasing the number of defects. However, the scanning microscope images show no visible change in either the shape of the particles or the homogeneity of the array. Furthermore, the small reduction of the sample homogeneity can reduce slightly the decay time of the oscillations due to dephasing of the signals from different particles in ensemble
measurement. Nevertheless, it cannot explain the reduction of the period of oscillations. Most probably, the results could be explained by mechanical coupling between the particles and the ITO layer which significantly reduces the quality factor of the particle oscillations and changes the vibrational modes.

In the second set of experiments, we study how the presence of a thin metal layer over an array of particles affects their lattice vibrations. Firstly, we evaporated a 5 nm silver layer on top of the array of 70 nm thick silver NSL particles formed with 780 nm diameter spheres. Depositing silver at thickness below ca. 20 nm does not produce a uniform continuous film, instead either an array of separated nanoparticles or connected structures are formed (for more details see Chapter 4). Our experimental data show that deposited silver layer suppresses the oscillations in the transient transmission signal (Figure 3.8a). This probably means that the deposited material either significantly decreases the quality factor of the particle vibrations or increases the inhomogeneity of the array, shortening the decay time of the oscillations in ensemble measurements.

![Figure 3.8](image_url)

**Figure 3.8.** a) Differential transmission measurements on arrays of 70 nm thick silver NSL particles made by spheres with diameter 780 nm. The black line shows a single frequency oscillation signal which nearly vanishes when 5 nm silver layer is deposited on top of the array (red line). b) The transient transmission signal from array of 100-nm-thick silver particles made by 780 nm polystyrene spheres. The black line represents the signal from the bare array; the red line shows the signal from particles covered by 0.2 nm AuPd layer. The top inset is the extinction spectrum of 0.2 nm AuPd layer on glass substrate. Bottom inset shows extinction spectra of the bare particles array (black) and that covered with 0.2 nm AuPd layer (red).

To rule out one of these hypotheses, namely the inhomogeneity of the sample, we fabricated another sample with reduced thickness of the deposited metal layer. Since the silver or gold does not form a continuous film at small
Acoustic oscillations

thicknesses, we sputtered AuPd layer on top of 100-nm-thick silver particles made by NSL technique with 780 nm spheres. The signal from the covered sample is compared with that from the bare particle array. The scanning microscope images show that sputtered AuPd layers with thicknesses of order of 1 nm form uniform films containing nanometer-sized grains.

To find out how the deposited metal layer affects the particles LSPR, we measured the transmission spectra for an ensemble of particles using a spectrophotometer (bottom inset in Figure 3.8b). The results reveal 20 nm red shift of the plasmon resonance with no detectable broadening of the resonance shape. In addition, the extinction spectrum of AuPd film of the same thickness on glass substrate shows a negligibly small absorption over the whole visible spectrum proving an extremely small thickness of the film. The results indicate that the thin metal layer does not change significantly the particle plasmon resonance and thus does not alter strongly the inhomogeneity of the array. However, the transient transmission measurements reveal significant changes in the signal due to the presence of the film. Thus, amplitude of the oscillations is dropped and the decay time became much shorter than in the case of bare particles.

One can argue that the vanishing of the oscillations may be due to a shift of plasmon resonance in such a way that the probe wavelength coincide with the wavelength of LSPR, which may change the amplitude of the oscillations or even cause the complete disappearance of the oscillations in signal. However, if this were the case there would be no acoustic peaks in the signal and the signal would be flat except for the first bleach [41]. In our data, the two first oscillation peaks are clearly visible, which indicates that the reason for vanishing of the signal is a rather short decay time. The results of the study show an extremely strong sensitivity of the mechanical vibrations of nanoparticles to the environment, which indicates that the transient transmission measurements may be used for sensing applications.

3.4 Summary and conclusions

In this Chapter we demonstrated that the transient optical transmission measurements can be used for non-contact investigation of the elastic properties of nanoparticles. In addition, the high sensitivity of the particle
response to changes in its environment allows for investigation of the energy transfer between the particles and the surrounding media.

In our experiments we studied the effects of the incident optical intensity on the response of the particle arrays and showed that for a certain range of incident intensities the amplitude of oscillation scales linearly with the applied optical intensity. Furthermore, the maximum intensity at which the signal starts saturating has been determined.

We also measured the dependence of the period of the particle oscillation on the particle thickness. The weak dependence of the vibrational period indicates the lateral character of the particle deformations. In addition, we showed that for particles with high aspect ratio of height to lateral dimensions extra vibrational modes, apart from the lowest fundamental, are excited.

We studied the effect of the particle’s shape on its vibrational response. The shape of the fabricated particles was altered by means of a modified NSL technique, in which a continuous reduction of the sphere diameter in the lithographic mask allows for a transformation of the arrays of particles into a film perforated with nanoholes. Experiments show that particles with extended tails have the same period of oscillation as non-modified ones. This counter-intuitive result probably means that the tips of triangular shaped particles do not play a significant role in fundamental vibrational mode. In addition, the experiments on films perforated with nanoholes show no pronounced oscillations.

We showed that the vibrational particle response strongly depends on particle’s symmetry. The particle arrays were fabricated by AR NSL technique which allows one to create particles with a distorted shape. We have shown that even minor asymmetry in the particle’s shape causes a significant change in the decay time of the oscillation with much smaller change in the vibrational period.

The effects of the environment on the quality of the particle vibrations were studied. In particular, we showed that ITO substrate significantly reduces the quality factor of the particle oscillations and modifies the excited vibrational modes. Furthermore, the experiments with thin metal overlayers reveal an extremely strong sensitivity of the particle response to such an environment making the system attractive for sensing applications.
A THz gap [72] has been highlighted in the electromagnetic spectrum, due to a lack of traditional sources and detectors in the frequency region from ca. 0.1 to 10 THz. This situation has begun to change in recent years, with the development of free-electron lasers [72, 73], quantum-cascade lasers [74], and table-top spectrometers based on ultrafast laser pulses [75]. THz radiation via ultrafast laser irradiation has been shown to happen via various mechanisms: optical rectification in nonlinear dielectric materials [76], photoexcited plasmas in gases [77], demagnetisation in ferromagnets [78] and via the surface field emission and photo-Dember effects in semiconductors [79, 80], amongst other mechanisms.

In this Chapter we report on an investigation of the generation of THz pulses in plasmonic structures irradiated by femtosecond laser pulses. The results are analysed in the context of a model in which photoelectrons are produced by plasmon-mediated multi-photon excitation, and THz radiation is generated via the acceleration of the ejected electrons by ponderomotive forces arising from the inhomogeneous plasmon field. In this study we explore the dependence of the THz emission on the femtosecond pulse intensity and on the metal nanostructure morphology. By comparing the measurements to numerical modelling, we are able to verify the role of the particle plasmon mode in this process.

4.1 THz generation from metal surfaces

The fields of nanophotonics, near-field optics and plasmonics all seek to harness light at the sub-wavelength scale. Plasmonics, in particular, offers the prospect of deep sub-wavelength confinement of light and an associated enhancement of the electromagnetic field strength. These attributes enable an increasing number of applications to be pursued, ranging from data storage [81], therapies for cancer [82], and the generation of deep-UV/soft X-rays by high-harmonic generation [83].
Whilst many applications exploit the spatial confinement and field enhancement in the vicinity of plasmonic metal nanostructures, much less attention has been given to the field enhancement that occurs inside the metal. One phenomenon which hinges on this effect is the photoemission of electrons from nanostructured metals after excitation by ultrashort laser pulses. Several studies have investigated such ultrafast photoemission from planar films [84], semi-continuous metal films (SMFs) [85], metallic gratings [86, 87], and nanoparticles [88]. In each of these studies, photoemission processes were supposed to be controlled by plasmon modes associated with the metal surfaces. It is thought that the role of the plasmon is two-fold: high electric fields inside the metal can explain observed enhancements in photoemission after excitation on resonance with plasmon modes, whilst high field-gradients are thought to induce charge acceleration through the ponderomotive force [89], giving rise to high-energy photoelectrons [90].

Such a rapid burst of high energy photoelectrons could possibly be accompanied by the emission of THz radiation. THz emission following the illumination of nanostructured metal surfaces by femtosecond laser pulses has been observed from planar (rough) metal films [91, 92], and corrugated films (gratings) [93, 94]. In this Chapter we provide the first reproducible experimental evidence that supports the recent predictions [95] of THz emission from metallic nanoparticles. We investigate two sample types, SMFs and ordered arrays of metal nanoparticles produced by NSL technique. SMF exhibit more intense THz emission. However, owing to the inhomogeneous nature of these metallic nanostructures, they are not an easy platform upon which to explore the underlying physics. Ordered arrays of metallic nanoparticles allow us to overcome this problem since these structures have the important advantage that their electromagnetic response can be modelled in detail. By exploring the dependence of the THz emission as a function of metal nanoparticle morphology and dimensions, and by comparing measurements to electromagnetic modelling, we are able to confirm the role of particle plasmon modes in the THz emission process.

### 4.2 Semicontinuous metal films

When the metal is deposited at small thicknesses (below 20 - 30 nm) on glass substrate, the metal does not properly wet the substrate surface and so a
THz generation from plasmonic structures

continuous film does not form. Instead, surface tension leads to the formation of different types of structures. The morphology of the structure depends on the conditions of metal deposition, type of substrate used and the amount of evaporated metal. At small thicknesses the deposited metal is irregularly dispersed over the substrate islands (Figure 4.1a). Increasing the amount of deposited metal results in these islands growing (Figure 4.1b) and then they start to coalesce, forming a network of metal structures with bridges and gaps. As the film grows, more and more fragments accrete and finally at some point all the cluster parts become interconnected (Figure 4.1c).

![SEM images of silver SMFs with different thicknesses. The magnification is 100000. Light grey colored areas in micrographs represent silver. The films are evaporated at a rate of 1 Å/s. The mass-thicknesses are 5 nm for (a), 10 nm for (b), 15 nm for (c), and 20 nm for (d). The scale bar is 500 nm.](image)

The transition from a disconnected structure to a connected one occurs when the metal concentration $p$ exceeds a critical value $p_c$ which is called the percolation threshold. At this concentration the morphology of the system
undergoes a geometrical type phase transition. This leads to an abrupt change of the electrical conductivity at the percolation threshold (Figure 4.2a), so the system shows a dielectric-like behaviour at $p < p_c$ and metal-like behaviour at $p > p_c$.

At higher surface coverage all the gaps are filled with metal and a continuous metal film is formed (Figure 4.1d). With alteration of the metal concentration the optical response of the structure significantly changes. Thus at small concentrations when the structure consists of small disconnected metal islands the transmission spectrum resembles the spectrum of small metal nanoparticles (Figure 4.2b). At concentrations $p > p_c$ the transmission spectrum is similar to that of continuous metal films (Figure 4.2b).

![Figure 4.2](image)

Figure 4.2. (a) Measured resistivity of silver films as a function of mass-equivalent thickness. The films are evaporated at a deposition rate of 1 Å/s. (b) Extinction spectra of silver films with different thicknesses. Spectra are taken by microspectroscopy with an objective Nikon ×40 (NA 0.60, S Plan Fluor ELWD) in TBF.

It was shown in many studies that near the percolation threshold SMFs are able to localise the electromagnetic field in small nonometer-sized areas, “hot spots” [96], [97], with strongly enhanced local fields relative to applied field. The large local fields lead to the enhancement of various optical phenomena, such as surface-enhanced Raman scattering (SERS) [98–101], second and third harmonic generation [102, 103], emission of electrons [85] and THz generation [104, 105], amongst others.

There are several techniques to “visualise” the “hot spots”. One of them, near-field scanning optical microscopy (NSOM), is widely used to probe the near fields with subwavelength resolution [106–109]. The results obtained from near-
THz generation from plasmonic structures

Field optical microscopy are in agreement with theoretical considerations of such random metal-dielectric systems and show the presence of small local areas with high electric field [110, 111]. It is interesting that the pattern of strong field localization greatly varies with excitation wavelength and does not simply correlate with the film topography [112]. Though the average field enhancements in percolation films are large, a factor of ~ $10^2$, they are much smaller than the peak values in hot spots, of order of $10^4$ [113]. This is because of the large spatial separation of the sharp peaks giving significantly reduced averaged values.

Another technique used for visualising hot spots in metal-dielectric composites is photoemission electron microscopy (PEEM) [114]. The advantages of this technique include the absence of any perturbation from the fibre tip on the system and the ability to map hot spot patterns with a spatial resolution as high as 20 nm. Also, great achievements were obtained in modelling real semicontinuous metal films 3D finite-difference time-domain (FDTD) method, which gives a good agreement with experimental results [115, 116].

4.3 THz generation from semicontinuous metal films

For the generation and detection of THz pulses, a THz time-domain spectroscopy setup was employed. The details of the setup can be found in Chapter 2. In the standard THz-TDS setup for the generation and detection of THz radiation, nonlinear crystals with a high second-order susceptibility are used. One such crystal, ZnTe, was used in our experiments for the detection of THz pulses and also for their generation as a reference source. For experiments on THz generation from other structures, such as metal films, nanoparticles etc., the ZnTe crystal used for generation of THz pulses is replaced by the sample under investigation. In this section we describe the experimental results of THz generation from SMFs. The time-domain signal obtained from a silver SMF is shown in Figure 4.3a. For comparison, the data for ZnTe crystal are shown on the same plot. The spectrum of the generated THz radiation is obtained by a Fourier transform of the time-domain signal (Figure 4.3b). The signals are in the ~ 1 THz range owing to the duration of the excitation pulses we employ. To compare the strength of the signals from different sources or at different generation conditions, one needs to evaluate the overall intensity of the THz radiation. The strength of the THz electric field can
be found by integrating the spectrum of the generated THz pulse and the intensity is then obtained by squaring the field strength.

![Time-domain measurements of emitted THz pulses](image)

Figure 4.3. (a) The representative time-domain measurements of emitted THz pulses after optical excitation of 1 mm thick ZnTe crystal (black) and 15 nm thick silver SMF (red). For the sake of comparison the signal from ZnTe crystal is scaled down by a factor of 10. (b) Spectra of emitted THz pulses obtained by applying the Fourier transform to the data in (a).

### 4.3.1 Film thickness dependence

Semicontinuous films were fabricated by evaporation of a metal under vacuum onto glass substrates at a pressure of $< 10^{-5}$ mbar. A range of samples were made, using both silver and gold, altering the mass of the metal deposited and also the deposition rate. We refer to the different films by their mass-thickness, the equivalent thickness of metal that would have been produced had the film been continuous. Sample morphology is characterised by scanning electron microscopy, and the linear optical response assessed by acquiring extinction spectra. Examples of extinction spectra and of an SEM image of a sample near to the percolation threshold are shown in Figure 4.4.

Examination of the SEM images for the different samples indicates that the percolating structures have many small gaps (see Figure 4.4). As it was discussed in the previous section, many studies of SMF show the high field enhancements associated with such gaps. Although the extinction spectra corresponding to percolating samples do not show a well defined plasmonic resonance, this does not mean that plasmonic resonances are not present [97], [111]. The illumination of the sample with laser pulses at certain wavelength excites corresponding resonances and creates hot spots with highly enhanced electric field. As it was shown, the highest local fields are achieved for the samples near to percolation threshold [111, 117]. Thus this range of film
THz generation from plasmonic structures

Thicknesses is the most interesting for applications relying on enhanced local fields. However, the percolation threshold is not a constant for a given material, but rather depends on the fabrication conditions and the type of substrate [118]. To investigate how the THz intensity depends on the film morphology, we performed THz generation from films with thicknesses in the range 8 – 20 nm of silver and 8 – 15 nm of gold deposited at a rate of 1 Å/s and silver films with thicknesses 18 – 25 nm deposited at a rate of 0.1 Å/s.

4.3.1.1 Silver and gold films, deposition rate 1 Å/s

Figure 4.4. (a) Extinction spectra of silver SMFs with different mass-thicknesses near to percolation threshold deposited at a rate of 1 Å/s. The spectra are acquired by spectrophotometer. (b) SEM micrograph of percolating silver film, mass-thickness 12 nm (the darkest regions indicate the absence of metal).

The measured THz intensity as a function of mass-thickness of a number of silver and gold SMFs is shown in Figure 4.5; the intensity of the pump pulse was 5 GW/cm², and the sample was illuminated at an angle of ~ 40°. We can see that the THz emission is maximal for mass-thicknesses of ~ 13 nm. We observe a similar dependence for gold samples, with a peak at a mass-thickness of ~ 10 nm. It is interesting to note that, for both silver and gold, the strongest THz signal occurs for samples with a thickness slightly above the percolation threshold, as determined via resistivity measurements (Figure 4.1a). We correlate these observations with the associated extinction spectra from the samples. For silver films the extinction spectra shown Figure 4.4 exhibit particle plasmon-like resonances at film thicknesses below 11 nm. We observed similar resonances in gold films with thicknesses below 9 nm. At higher thicknesses the extinction spectra resemble those of continuous metal films. Furthermore, the analysis of SEM pictures corroborates the results of resistivity measurements.
and extinction spectra data, giving the thickness at the percolation threshold of around 11 - 12 nm for silver and around 8 - 9 nm for gold. These results agree well with previously reported data [119], though the exact threshold values depend on the deposition rate and the substrate material [99].

Figure 4.5. Measured THz intensity from semicontinuous silver (a) and gold (b) films as a function of the mass-thickness of the film. The films are evaporated at a rate of 1 Å/s. The samples were illuminated at angles of ~ 40°.

The evolution of the signal intensity for both investigated materials has common features: low signal at small and high metal thicknesses and a maximum of the intensity at the thickness slightly above the percolation threshold. The low intensity tails of the dependence are due to low field enhancement around the metal structures on both sides of the percolation threshold [120]. In addition, the silver films show a distinct feature close to the percolation threshold, where the dip in the intensity is observed. It is interesting to note that a similar behaviour of the field enhancement around the percolation threshold is theoretically predicted [96, 121] and corroborated by NSOM measurements [121]. In addition, in SERS experiments on silver SMFs the dip in the intensity at the percolation threshold is also observed [96]. In order to correlate the observed THz intensity dependence with the near-field enhancement, we performed SERS measurements on silver SMFs in a similar range of the metal concentrations (see section 4.3.2).

The different widths of the dependences (Figure 4.5) can be explained by the peculiarities of the film growth. Thus the transition from the separated particles to connected structure and subsequent formation of the continuous film occurs in a wider range of film thicknesses for silver than for gold. At the evaporation
rate of 1 Å/s the continuous metal film is formed at thicknesses above 20 nm for silver and 15 nm for gold.

It is interesting to note, that the high field-enhancement in SMF leads to a high electric field strength of the THz pulses emitted by these samples upon femtosecond laser pulse irradiation: the maximum field strength of such pulses is only a factor of 10 smaller than for pulses generated by optical rectification in a 1 mm thick ZnTe crystal under similar excitation intensities (Figure 4.3), despite a film thickness that is 5 orders of magnitude less than that of the crystal. Therefore, if optimized, particle plasmon structures may be practical as emitters in THz applications, especially where local THz emitters would be beneficial.

4.3.1.2 Silver films, deposition rate 0.1 Å/s

![SEM images of semicontinuous silver films with different thicknesses. The magnification is 150000. Light grey colored areas in micrographs represent silver. The films are evaporated at a rate of 0.1 Å/s. The mass-thicknesses are 18 nm for (a), 20 nm for (b), 22 nm for (c) and 25 nm for (d). The scale bar is 500 nm.](image-url)
We showed above that the maximum THz intensity is reached for both silver and gold films slightly above the percolation threshold. However, in order to get an insight into the phenomena, it would be beneficial to clarify the link between the film percolation threshold and the maximal signal of THz generation. Since the film growth conditions depend on the parameters of the film deposition, it is possible to shift the percolation threshold by altering the deposition rate, keeping all other parameters constant. For this experiment we prepared a set of silver films evaporated on glass substrates at a deposition rate of 0.1 Å/s. In accordance with [118] this should lead to a higher thickness at the percolation threshold.

Examination of SEM images (Figure 4.6) of the films reveals that the percolation threshold for this deposition rate is ~ 20 nm, which is about twice as thick as the percolation threshold for films evaporated at a rate of 1 Å/s. We correlate these observations with associated extinction spectra, which indicate that the transition from the particle-like to film-like response occurs at the silver thickness ca. 20 nm.

Figure 4.7. (a) Measured THz intensity from silver SMFs as a function of the mass-thickness of the film. The films were evaporated at a rate of 0.1 Å/s. The samples were illuminated at angles of ~ 40°. (b) Extinction spectra of these silver films. The spectra are acquired by spectrophotometer.

Figure 4.7a shows the measured THz intensity as a function of mass-thickness of a number of silver SMFs, the intensity of the pump pulse was 20 GW/cm², and the sample was illuminated at an angle of ~ 40°. From the data it can be seen that the THz signal maximizes at a mass-thickness of 22 nm. This value is slightly above the percolation threshold (20 nm) in accordance with the results on silver and gold SMFs evaporated at a deposition rate 1 Å/s. These results are also in agreement with THz measurements on gold SMFs reported in [104].
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In that paper, THz radiation was generated in a reflection configuration, opposite to our transmission setup. Thus, we can assume that the fact of reaching the maximum of THz intensity at the metal thickness slightly above the percolation threshold is rather universal and does not depend on the generation configuration or conditions of film fabrication.

4.3.2 SERS measurements on silver SMFs

Surface-enhanced Raman spectroscopy is a powerful tool for sensing the local electromagnetic fields. The technique is based on measuring Raman scattering, i.e. inelastic photon scattering, from the molecules linked to an object under investigation. The SERS was firstly discovered by Fleischmann et al. in 1974 [122], though the correct interpretation of the phenomena was done in 1977 [123, 124]. For the last thirty years the field has grown enormously and now finds the numerous applications in physics, chemistry, biology and plasmonics. The Raman scattering is a weak process, however the presence of a metal surface with high local fields strongly enhances the signal, with an amplification as much as 10 - 11 orders of magnitude possible [125, 126], which makes it possible to detect a scattering signal even from a single molecule [126, 127].

It is the effect of the Raman signal enhancement in the presence of a metal surface that arguably made the SERS technique so attractive for many research disciplines. If considered in the simplest way, the SERS enhancement in the presence of the metal surface depends on two effects, excitation enhancement and re-emission enhancement. The enhanced local field $E_{loc}$ induces an amplified Raman dipole with the polarizability proportional to the field strength. Thus the energy radiated by such a dipole is enhanced by a factor of $E_{loc}^2(\omega_k)/E_0^2$, where $\omega_k$ is the excitation wavelength and $E_0$ is the incident field strength. The presence of the metal surface with enhanced local fields affects not only the excitation of the Raman dipole, but also its emission. In order to estimate this effect it is often assumed that the re-emission enhancement factor is of order of $E_{loc}^2(\omega_R)/E_0^2$ [128], where $\omega_R$ is the dipole radiation wavelength. Since the shift in the wavelength during the Raman scattering is small, $\omega_R \approx \omega_k$, the expression for SERS enhancement factor (SERS EF) takes the form...
$SERS\ EF = \frac{\left| E_{\text{lo}}(\omega_L) \right|^4}{\left| E_0(\omega_L) \right|^4} = EF^4,$

(4.1)

where $EF$ is a local field enhancement factor. The last expression is the most known SERS EF approximation, which shows the fourth power dependence of SERS enhancement on the local plasmonic field. So, the high-order dependence explains the extremely strong signal amplification measured in SERS experiments. Thus, a local field enhancement of 2 orders of magnitude causes 8 orders of magnitude amplification in SERS signal. For us the most important fact about SERS is the power-like dependence of the SERS signal on the enhancement of the local field. This relation makes it possible to restore the dependence of the average electric field enhancement from the SERS signal dependence for a set of samples.

Figure 4.8. SERS spectra of a thiophenol monolayer on 12 nm silver SMF taken with two different laser wavelength 532 nm (black) and 785 nm (red). The spectra are shown in the range of shifts from 500 cm$^{-1}$ to 2000 cm$^{-1}$ (a) and with zoomed peaks at 997, 1020 and 1070 cm$^{-1}$ in the range of shifts from 980 cm$^{-1}$ to 1100 cm$^{-1}$ (b). The red curve is offset for clarity.

In our experiments the SERS signal was measured from thiophenol molecules attached to silver films. To fabricate the samples we covered the evaporated silver SMFs with thiophenol monolayers using the procedure described in [129], which includes the following steps. Freshly prepared silver films were rinsed in absolute ethanol for 1 min to remove any surface contaminants. The cleaned films were then immersed in ethanolic solution of 10 mM thiophenol for 60 min. After the formation of thiophenol monolayers, the samples were rinsed in ethanol again with subsequent drying in a nitrogen stream. Then the SERS signals from the samples were analysed at two excitation wavelengths 532 nm and 785 nm.
In Raman spectroscopy the spectrum of the scattered light is plotted in units of the wavevector shift of inverse cm. The SERS signals measured from thiophenol monolayers on 12 nm silver film at two excitation wavelengths, 532 and 785 nm, are shown in Figure 4.8. The most prominent peaks are assigned to the following molecule vibrations: 650 cm\(^{-1}\) (CS stretching mode), 997 cm\(^{-1}\), 1020 cm\(^{-1}\) (CC stretching mode), 1070 cm\(^{-1}\) and 1570 cm\(^{-1}\) (CH stretching mode) [130–132]. Investigation of the Raman scattering intensity for a number of silver SMFs was based on the strength of the peak at 997 cm\(^{-1}\).

Figure 4.9. SERS signal from thiophenol monolayers on silver SMF as a function of the film mass-thickness acquired with two excitation wavelength, 532 nm (a) and 785 nm (b).

The Raman signal is measured from silver films with thicknesses in the range from 5 nm to 20 nm with two excitation wavelengths 532 nm and 785 nm (Figure 4.9). While the signal strength varies with the wavelength, there are common features: the local minimum in the signal from 11 nm thick film and a nearly monotonic tail for films with high thicknesses. There is also a tail in the dependence at small film thicknesses on Figure 4.9b which is not so prominent in Figure 4.9a. The most interesting peculiarity of both dependences is a dip for a percolating sample (11 - 12 nm). The near-field distribution study [117] shows that, while the density of hot spots is maximal in percolating samples, the local field enhancements are lower than that for the films with metal concentrations slightly away from the percolation threshold. The theoretical [96, 121] and experimental, NSOM [121] and SERS [101], investigations of the local field distribution as a function of the metal density show two peaks in the average field enhancement for silver films with a dip at the percolation threshold. The shape of the peaks and the dip varies with wavelength, becoming more
prominent at higher wavelengths [96] in agreement with our SERS measurements.

Let us now turn to a comparison of THz (Figure 4.5a) and SERS (Figure 4.9b) results. Since the excitation wavelengths are close to each other, 800 nm and 785 nm for THz and SERS measurements respectively, the average local field enhancements should be similar in both cases. These two signal dependencies show similar behaviour at the film thicknesses around the percolation threshold: a dip in the signal for the percolating sample with two local maxima, one on each side of the percolation threshold. In addition, there is a signal decrease for small and high film thicknesses with an absolute maximum at the thickness slightly above the percolation threshold. This shows that the plasmon field enhancement plays an important role in generation of THz radiation from such structures.

4.4 THz generation from arrays of nanoparticles

In the previous section we showed that THz generation from plasmonic structures strongly depends on the field enhancement in the vicinity of the metal surface. To get further insight into the phenomenon and to optimize the effect of THz generation, one needs to be able to correlate THz emission with sample morphology, and in particular to be able to determine local field enhancements. This is very difficult for SMF, but this difficulty can be overcome if we investigate well-defined, ordered nanoparticle arrays. The spectral position of the plasmon modes supported by metallic nanoparticle arrays can be controlled by varying the size, height and spacing of the metallic nanoparticles. As in the case for the SMF, extinction spectra allow us to monitor the plasmon modes supported by the different particle array structures we fabricate (Figure 4.10a and Figure 4.11a).

4.4.1 LSPR resonance position, experimental results

To investigate the dependence of the generated THz intensity on the relative positions of the excitation wavelength and the plasmon resonance, we made experiments with two sets of samples. The first set consists of NSL particles of the same height but different lateral dimensions. This is done by using polystyrene spheres with different diameters of 390 nm and 780 nm as a lithographic mask, which leads to a roughly twofold change of the particle lateral
dimension. As a result, these two arrays have the plasmon resonances at ~550 nm and ~830 nm for small and big particles, respectively (Figure 4.10a). Since the excitation wavelength is ~800 nm, one should expect a lower field enhancement in the vicinity of the smaller particles and hence a weaker THz signal. The results of THz generation experiments are in agreement with the expectations, giving about 15 times smaller THz intensity (~4 times in electric field strength) from the sample with a plasmon resonance at ~550 nm than that from the sample with a plasmon resonance at ~830 nm for the same incident intensity, ~5 GW/cm² at an angle of 40° (Figure 4.10b). These results suggest that THz emission is enhanced when the wavelength of the plasmon resonance matches the incident wavelength.

Figure 4.10. (a) Optical extinction spectra from NSL particle arrays fabricated using spheres with diameters of 390 nm (blue) and 780 nm (red) and thickness of silver layer of 60 nm. The spectra are acquired by microscope spectrometer in the TBF mode. The vertical line shows the position of the laser wavelength. (b) Spectra of emitted THz pulse from 1 mm thick ZnTe crystal (black) and NSL particles made using spheres of 780 nm (red) and 390 nm (blue) in diameter. For the purpose of comparison the signal from ZnTe is scaled down by factor of 100.

To further explore this relationship between plasmon resonance and THz emission, we created a second set of different nanoparticle arrays. Each was produced using the same diameter polystyrene spheres (780 nm), differing only in the thickness of the silver layer. Extinction spectra for arrays with thicknesses of silver in the range 20 – 150 nm are shown in Figure 4.11a. The largest peak in the extinction corresponds to the dipolar plasmon resonance of the particles [133]. The dependence of the LSPR peak wavelength versus the particle height is plotted in the inset of Figure 4.11a. Increasing the thickness (height, h) of the particles results in a blue shift of the plasmon resonance, in agreement with the published results for silver NSL particles, [63], though the reported height
sensitivity factor (7) in a similar spectral range is much higher than that obtained in our experiments (~ 2). The spectra indicate that the plasmon resonance for short particles of 20 nm height is at ~ 900 nm, on the long wavelength side of the illumination wavelength (~ 800 nm). As the height of the particles is increased, the resonance is shifted to shorter wavelengths. For particle height between 60 and 70 nm the resonance wavelength matches the wavelength of the incident pulses. The intensity of the THz emission is shown as a function of particle height (thickness) in Figure 4.11b. Two sets of data are shown, one set was obtained for pulses normally incident on the array, the other for pulses incident at an oblique angle of ~ 40° (as discussed below, the THz emission is much stronger when samples are illuminated away from normal incidence). We observe in both data sets a maximum in THz emission for arrays with particle height (thickness) ~ 50 nm, close to the condition of resonant excitation. This implies that the excitation of the particle plasmon resonance by the incident laser pulse enhances the THz emission process.

Figure 4.11. (a) Optical extinction spectra from NSL particle arrays of various thicknesses. The spectra are acquired by microscope spectrometer in the TBF mode. The lithographic mask was made of spheres with diameter 780 nm. Data are shown for particle heights of: 20, 30, 40, 50, 60, 70, 100 and 150 nm, the arrow shows the direction of increasing particle height. Inset: plot of plasmon resonance peak wavelength versus the particle height. The solid line represents the linear fit to the data. (b) Dependence of THz intensity on the thickness of particles made by using spheres with diameter 780 nm. Two sets of data are shown, full line (circles) are for normally incident excitation, dashed line (crosses) are for oblique excitation, at an angle of 40°. The lines are included solely as guides the eye. The incident intensity in both cases was ~ 5 GW/cm².

4.4.2 Particle thickness, computer modelling

In order to gain insight into the physical origins of this observed height dependence of the THz emission, the electromagnetic modelling [134, 135] is
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carried out using the finite element method (FEM) (HFSS v.13, Ansoft Corporation). The results from computer modelling were obtained by Dr. Edmund Stone, the author greatly appreciates this contribution.

The 3D model [136] employs the rhombic unit cell of the arrays, as shown in Figure 4.12. Spatial dimensions for the unit cell and the particles are taken from SEM images. The model employs ~ 15000 tetrahedral elements per particle, and solutions were sought following adaptive procedures to optimize the meshing. Particle edges were rounded to a radius of 3 nm. Note that the substrate was excluded from our model since its presence leads to the existence of propagating diffracted orders which significantly complicates the calculation, making convergence too computationally intensive for the available computing resources. Both reflection spectra and the spatial distribution of the field strength were calculated (using a frequency dependent permittivity for silver [137]).

![Figure 4.12. Field distributions for a 40 nm thick pair of particles in a rhombic unit cell calculated using finite element modeling, after normal incidence light illumination with a wavelength of 800 nm. (a) Cross-section, (b) slice through center of plane of array. The E-field of the illuminating light is parallel to the line joining the particles. The point at which the field is calculated is shown in the inset to (a). The field is calculated in the plane parallel to the upper (flat) surfaces of the particles at the point where the corner of one of them would have been, had rounding of the tip not been implemented. The plots show the time-averaged magnitude of the electric field.](image)

The calculation shows that the local electric field is highly inhomogeneous with strong localization in the areas of the highest field enhancement. To compare the strength of the local fields for different structures one has to calculate a representative value of the field enhancement for each system. One of the possible approaches is to calculate an integrated field enhancement throughout a plane or a volume around the particle. However, due to different heights of the compared particles, this approach fails. If one chooses to integrate the local fields over the plane, the distance from the plane to the regions of the highest
electric field changes with the particle height. In the case of the volume integration approach, the amount of the metal in the integrated volume changes with the particle height.

Figure 4.13. Results from numerical modelling. Left panel (a): shows how the calculated reflection spectra change with varying particle height. Data are shown for height values of: 20, 30, 40, 50, 60, and 90 nm, the arrow shows the direction of increasing particle height. Right panel (b): the dependence of the maximum field enhancement (located close to the facing tips) on particle height.

Another method which avoids this problem is to compare the highest field enhancements for each particle, which are found at the vertices of the particles along the polarization axis of the illumination (Figure 4.12). The absolute values of the field enhancement are calculated by normalizing the local fields to the incident field strength. Our calculations (Figure 4.13b) indicate that the optimum particle height in terms of field enhancement occurs when the plasmon resonance is close to the incident wavelength. However, closer inspection of the data shows that the extinction maximum seems to be slightly red-shifted with respect to the maximum in THz signal (near-field enhancement). More specifically, while the particle height of 50 nm gives the greatest field enhancement (Figure 4.13b), for this particle height the calculated plasmon resonance peaks at 810 nm, whereas the pump is centered at 800 nm. This shift appears more strongly in the experimental data. Also, the particle height of 50 nm gives the strongest THz signal when pumped at 800 nm, see Figure 4.11b, but for this particle height the extinction peaks at 860 nm, see Figure 4.11a. This shift is of the opposite sign to that seen in fluorescence enhancement studies [138, 139]. It is possible that the sign of the shift depends on the shape of the particle [128] but this aspect needs further investigation to clarify the physics behind the shift we observe. In addition, it is interesting to note that in recent SERS experiments it was shown that the highest Raman
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scattering enhancement is observed when the plasmon resonance is red-shifted to the excitation wavelength [140].

An important trend is clear from our numerical modelling. The highest field enhancements are generated both inside and outside the particles corresponding to the samples from which we observe the highest THz emission; an example of the calculated field enhancement distribution is shown in Figure 4.13. The plasmon resonance clearly plays an important part in the emission process. However, the mechanism of THz generation is still not clear. To address this point we investigate the dependence of the THz emission on the intensity of the incident pulses.

4.5 THz intensity dependence

In Figure 4.14 we plot the emitted THz intensity as a function of the optical excitation intensity for two samples. The first sample, array of NSL nanoparticles, is fabricated using spheres of 780 nm diameter with the thickness of the deposited silver layer of 50 nm. The second sample is a semicontinuous silver film. The power dependences of THz radiation from plasmonic structures are compared to that from a ZnTe crystal, a commonly used source for THz generation by optical rectification [141].

To analyze the results of the intensity dependence measurements we fit the experimental data with a power function. We will call the value of the exponent of this power function the (effective) order of the process, or more simply, the order dependence. The THz intensity from the ZnTe crystal shows an approximately 2nd order dependence on the pump intensity as expected for optical rectification process (the dependence is somewhat sub-second order, as has been observed in this range of incident intensities [44]). For optical intensities below 5 GW/cm² the THz intensity from the plasmonic structures shows a 5th (6th for percolating film) order dependence on the optical pulse intensity for the NSL particles (SMF), dropping to less than 2nd order for intensities in the range from 5 GW/cm² to 20 GW/cm². For optical intensities above 20 GW/cm² the intensity dependence saturates. It is important to note that for incident optical intensities below 5 GW/cm² the dependence is significantly different from the more common 2nd order THz generation mechanisms, such as optical rectification. However, similar bimodal intensity dependences have also been observed in ultrafast photoemission...
measurements. For example, the order of the intensity dependence of the photocurrent exhibited by a flat silver surface excited by femtosecond pulses in the Kretschmann geometry was observed to vary from about 3 for intensities below 4 GW/cm$^2$ to about 1.5 for intensities above 8 GW/cm$^2$ [142]. This suggests a link between photoemission and THz generation. Indeed, the order of the process for the generation of THz radiation from a one dimensional diffraction grating in gold has been observed to vary from 3.5 to 2.0 on increasing the intensity of photoexcitation over a similar range [94]. We note that the recent work of Ramakrishnan and Planken [104] on semicontinuous gold films does not show a bimodal intensity dependence; however, their conditions were somewhat different, notably they used a lower pump intensity but a higher average power.

![THz Intensity vs. Incident Intensity](image)

Figure 4.14. Emitted THz fluence as a function of the optical excitation intensity for (lower data set) an NSL array produced using spheres of 780 nm diameter, and 50 nm silver layer; (middle data set) a percolating silver film of equivalent mass-thickness of 15 nm; and (upper data set) optical rectification of ZnTe. The numbers in the brackets are the fitted “orders” of the lines associated with the data.

Many of the main properties of the measured THz emission (such as the unusual intensity dependence shown in Figure 4.14) can be accounted for within the following model, based upon that of Welsh et al. [93]:

\[
\begin{align*}
\text{Thz Intensity (a.u.)} & \quad \text{Incident intensity (GW/cm}^2\text{)} \\
\text{Particles} & \quad (5) \\
\text{Film} & \quad (1.75) \\
\text{ZnTe} & \quad (1.5)
\end{align*}
\]
i. Particle-plasmon excitation and multiphoton absorption of light leads to enhanced electromagnetic fields around the particle and to the ejection of electrons from the metal.

ii. The ejected electrons are subject to forces exerted on them by the electromagnetic field; in our case this is primarily the field enhanced by the particle plasmon resonance.

iii. Since the electromagnetic field associated with the plasmon resonances is localized in the close vicinity of the particles the field is inhomogeneous. This inhomogeneity leads to ponderomotive acceleration of the electrons [143]. The time scale of this acceleration is slow in comparison with optical period of the pump light and is determined by the spatial variation in the field. Moreover, the pulsed nature of the incident light means that the ponderomotive motion produces a time-varying current. The duration of the pulse (∼100 fs) means that the frequency of the ensuing radiation is of the order of 1 THz.

4.6 THz generation model

To expand on the link between photoemission and THz generation, we have developed a simple model to account for the intensity dependence of our THz signal. The evanescent electromagnetic fields associated with the plasmon mode have been suggested as being responsible for acceleration of the photoexcited electrons [93], and thus the emission of radiation. As noted above, for excitation by femtosecond laser pulses this emission lies in the THz band. One might expect the photocurrent, and hence the emitted THz electric field strength, to be proportional to the product of the number density, $N$, of the emitted photoelectrons and the acceleration, $a$, of the charges, i.e.

$$E_{\text{THz}}(I_{\text{opt}}) \sim \int_V \int_T N(l_{\text{opt}},t,r) a(l_{\text{opt}},t,r) d^3r \, dt,$$  

(4.2)

where $I_{\text{opt}}$ is the intensity of the pulsed excitation light, $T$ is a pulse repetition time and $V$ is a volume of the plasmon field.

The intensity dependence of the first term in equation (4.2) can be expressed in the form $N(l_{\text{opt}}) \propto I_{\text{opt}}^{n_i}$, where $n_i$ is the order of the multiphoton excitation. There are two distinguishing regimes defining the order parameter $n_i$ (by order we
mean the number of photons with energy 1.55 eV required to overcome the work function): multiphoton ionization ($\gamma >> 1$) and tunnelling ionization ($\gamma << 1$), where $\gamma$ is the Keldysh parameter \[144\],

$$\gamma = \frac{\omega (mA)^{1/2}}{eE_{SP}},$$ \hspace{1cm} (4.3)

where $\omega$ is angular frequency of the incident laser field, $m$ is the mass of an electron, $e$ is its charge, and $A$ is the work function of the metal (for silver $A = 4.1–4.7$ eV \[145, 146\]). The quantity $E_{SP}$ is the electric field strength of the evanescent plasmonic field in the vicinity of the nanoparticles. We write this field in the form $E_{SP} = \eta E_0$, where $\eta$ is the electric-field enhancement factor and $E_0$ is the strength of the incident electric field. Given that the incident intensity can be written as $I_0 = cE_0 E_0^2/2$, one can derive an expression for the incident intensity corresponding to $\gamma = 1$

$$I_{\text{opt}}^{\text{mpe}} = \frac{mAc_0 \omega^2}{2e^2 \eta^2}.$$

(4.4)

For low incident intensities, $I_{\text{opt}} < I_{\text{opt}}^{\text{mpe}}$, one expects multiphoton excitation of photoelectrons, characterized by an order parameter $n_1 = 3$, since the energy of three incident photons is required to overcome the work function. For higher intensities, $I_{\text{opt}} > I_{\text{opt}}^{\text{mpe}}$, one expects tunneling ionization to be the dominant mechanism of photoemission, characterized by an order parameter $n_1 = 1$. Thus, one can expect the order parameter for multiphoton excitation of photoelectrons to vary from $n_1 = 3$ to $n_1 = 1$ as the incident intensity is increased, with the transition between these regimes occurring near $I_{\text{opt}}^{\text{mpe}}$.

The intensity dependence of the second factor in equation (4.2), describing the acceleration of the emitted photoelectrons, can be expressed in the form $a(I_{\text{opt}}) \propto I_{\text{opt}}^{n_2}$. The order parameter $n_2$ may be estimated by considering the ponderomotive force which arises from the strong confinement of the evanescent plasmonic field. Though the spatial variation of the electromagnetic fields around our particles is very complex, for simplicity we will consider the plasmonic field to be uniform in the plane of the substrate and take the ponderomotive potential \[94\] to be of the form
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\[ U_{\text{pon}}(z) = U_0 \exp\left(-2z/\alpha\right), \tag{4.5} \]

where \( U_0 = e^2 E_{\text{sp}}^2 / (4m\omega^2) \), with \( z \) the direction normal to the surface, and where \( \alpha \) describes the evanescent decay of the plasmonic field. In addition, to simplify our approach, we ignore the change in the incident intensity during the pulse envelope. The ponderomotive force,

\[ F_{\text{pon}} = -\frac{dU_{\text{pon}}}{dz} = \frac{2U_0 \exp\left(-2z/\alpha\right)}{\alpha}, \tag{4.6} \]

gives rise to the acceleration of photoelectrons. From the expression above, (4.6), we see that there are two different regimes of acceleration: for small \( E_{\text{sp}} \) the acceleration of photoelectrons can be described as approximately uniform, with\[ a_0 = e^2 E_{\text{sp}}^2 / (2\alpha m^2 \omega^2) \]
over the duration of our excitation pulse, \( \tau \sim 100 \text{ fs} \). Such uniform acceleration occurs only over distances \( a_0 \tau^2 / 2 << \alpha \). Thus, one can define an incident intensity

\[ I_{\text{opt}}^{\text{pon}} = cE_0 \left( m \omega^2 / (t \eta \eta) \right)^2 = I_{\text{opt}}^{\text{mpe}} \frac{2m\alpha^2}{\lambda t^2}, \tag{4.7} \]

below which the acceleration may be considered uniform, and the ponderomotive force is unsaturated. For incident intensities greater than \( I_{\text{opt}}^{\text{pon}} \), one can expect non-uniform acceleration of photoelectrons. Thus, one expects the order parameter for acceleration to vary from \( n_2 = 1 \) to \( n_2 = 0 \) as the incident intensity is increased, with the transition occurring near \( I_{\text{opt}}^{\text{pon}} \).

To estimate the values \( I_{\text{opt}}^{\text{pon}} \) and \( I_{\text{opt}}^{\text{mpe}} \), one needs to know the values of the near-field enhancement factors. As it is mentioned, in our model we ignore the field distribution around the structure surfaces for simplicity. However, the local field distribution is strongly inhomogeneous, and thus it is not clear which value of field enhancement we should put in relations (4.4) and (4.7) to estimate the intensities \( I_{\text{opt}}^{\text{pon}} \) and \( I_{\text{opt}}^{\text{mpe}} \). It is noteworthy that, while both \( I_{\text{opt}}^{\text{pon}} \) and \( I_{\text{opt}}^{\text{mpe}} \) depend on the field enhancement factor, the ratio of these two intensities does not contain any information about the local field and thus less information is required to estimate one of the transition intensities if the another one is known.

To estimate this transition intensity we note from our modelling that typical field
decay lengths are $\alpha \sim 20 \text{ nm}$, in agreement with [135], and take the enhancement factor for our geometry from the literature [147] to be $\eta \sim 50$, consistent with our modelling (Figure 4.12). Using these values we find $I_0^{\text{mpe}} \sim 8 \text{ GW/cm}^2$ and $I_0^{\text{con}} \sim 1 \text{ GW/cm}^2$. This simple model therefore predicts that for incident intensities below $1 \text{ GW/cm}^2$ the system is in the regime of multiphoton photoemission ($n_1 = 3$) and an unsaturated ponderomotive force ($n_2 = 1$), so the total order parameter is $n_1 + n_2 = 4$. As the intensity of the emitted THz radiation is proportional to the square of the electric field, the dependence of the THz fluence as a function of the incident optical intensity is thus predicted to be 8th order in this low-intensity regime. For incident intensities between $1 \text{ GW/cm}^2$ and $8 \text{ GW/cm}^2$ the electrons are still liberated through multiphoton photoemission ($n_1 = 3$) but the ponderomotive force is partially saturated ($n_2 < 1$), so the total order parameter $n_1 + n_2$ is between 3 and 4. Thus, in this intermediate regime the THz fluence should be 6–8th order as a function of the incident optical intensity. According to our model, for higher incident intensities, approximately above $8 \text{ GW/cm}^2$, tunneling ionization and saturated ponderomotive force give rise to THz emission with a total order parameter of $n_1 + n_2 = 1$. Thus, the dependence of the THz fluence as function of the incident optical intensity is predicted to be a 2nd order in this high-intensity regime.

Let us now compare the experimental results (Figure 4.14) with this model. First, the model predicts an 8th order dependence of the THz fluence on the incident intensity at low incident intensities, something that we do not observe. We can understand why we do not see this 8th order dependence as follows. In our experiment we were not able to acquire low-noise data for incident intensities below $1 \text{ GW/cm}^2$, thus the low intensity regime in which the ponderomotive force is unsaturated and where an 8th order dependence is expected, is not available to us. It is interesting to note that the cross-over between $\sim 6^{\text{th}}$ and $\sim 2^{\text{nd}}$ order dependences in our experiment ($\sim 5 \text{ GW/cm}^2$ in Figure 4.14) occurs at approximately the intensity predicted for the transition between multiphoton to tunnelling regimes in our simple model, $\sim 8 \text{ GW/cm}^2$. This provides a strong evidence that the THz emission from our metallic
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particles is linked to the rapid burst of accelerated photoelectrons initiated by the ultrafast laser pulses.

4.7 Angle dependence

Even though each particle generates a pulse of electrons, the radiative THz emission for our samples will be determined by the entire array of particles. An understanding of how the electromagnetic fields generated by single particles add up in the far field is thus needed. Owing to the centrosymmetric nature of our arrays, the radiation emitted due to local ponderomotive currents in the plane of the substrate will cancel in the far field. Therefore, only out-of-plane components of the ponderomotive currents can contribute to THz emission. This effect can be observed in Figure 4.15, where we plot the THz intensity (measured in the direction of the excitation beam) as a function of the polar angle of incident light. For normal incidence, due to the absence of any phase retardation between the excitation of different particles, ponderomotive currents are not radiative and thus we should not expect THz emission. In the experiment, we observe a small residual THz emission at normal incidence, most likely due to inhomogeneities in the NSL arrays and/or the finite size of the excitation beam. Away from normal incidence, the THz emission increases. We stress that this effect has nothing to do with angle dependence of the field enhancement (indeed, our modeling suggests that the local field enhancement falls as one illuminates away from normal incidence).

In our experiments, we observe a maximum in the THz emission from all arrays for incident angles between 40° and 60°. One can qualitatively understand the origin of this maximum; as the angle of incidence increases, the magnitude of the out-of-plane component of the ponderomotive current capable of contributing to radiative emission increases as $\sin(\theta)$. In combination with this effect, sample rotation also increases the illuminated area of the sample and reduces the effective excitation intensity. One therefore expects the emitted THz radiation intensity to scale as $\cos^n(\theta)$, where $n$ represents the order of the THz (intensity) emission process. In this simple picture, the intensity of THz radiation is expected to scale as $\sin^2(\theta) \cos^n(\theta)$. One should note that such a simple picture is not complete as it ignores, for example, the angle dependent coupling of the incident light to the particle plasmon resonances. It does
however suggest that there will be an optimum angle for THz generation away from normal incidence, as seen in our experiments.

![Figure 4.15. Intensity of the emitted THz generation as a function of angle of incidence of optical pulses. The sample was made via the NSL technique, using 780 nm diameter spheres, the silver layer was 50 nm thick, and the incident laser power was 15 GW/cm². The inset shows the nature of the oblique illumination. Normal incidence corresponds to an angle of zero degrees.](image)

### 4.8 Summary and conclusions

In this Chapter we have reported our findings on the generation of THz pulses via irradiation of silver and gold SMFs and arrays of silver nanoparticles with femtosecond laser pulses. Our observations show that the high local fields in the vicinity of the plasmonic structures play an important role in THz generation from such structures. In particular, we have investigated the THz signal dependence on the thickness of silver and gold SMFs at metal concentrations close to percolation threshold, and correlated these results with SERS measurements on silver films. Our observations are in agreement with the reported investigations of near-field enhancement in such structures. To correlate the near-field strength and intensity of THz generation, we fabricated a set of NSL silver particles that allowed us to systematically vary the spectral position of the plasmon resonance. By varying the particle height and by comparing the modeled near-field strength with the intensity of THz emission we were able to show that the strongest THz signal is achieved from particles with the highest local field enhancement.

In addition, we investigated the dependence of THz fluence on incident optical intensity. Our results are consistent with a model in which THz radiation is
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produced by the emission of photoelectrons through multiphoton excitation and subsequent acceleration of these emitted electrons by ponderomotive forces associated with the optical fields of the plasmons in the metallic nanostructures. The simple model allowed us to account for the main observed features in the bimodal intensity dependence.

It is also interesting to note that the magnitude of the THz emission is remarkably large for an essentially 2D metamaterial, arising from an effective nonlinear polarization which is up to 4 orders of magnitude higher than in dielectric materials such as ZnTe crystal. There is therefore considerable scope to design 3D arrays of metallic nanoparticles, that is, metamaterials specifically designed to give optimal THz emission. As noted above, the centrosymmetric nature of our arrays means that THz radiation emitted due to local ponderomotive currents in the plane of the substrate will cancel in the far-field, designs employing noncentrosymmetric particles need to be investigated. Furthermore, attention to maximizing the field enhancement through particle design, and perhaps array design, where collective resonances [148] may play a role, are other avenues for future exploration. Finally we note that with some optimization it is plausible that one could use a single metallic nanoparticle as a local THz emitter.
Chapter 5
THz generation and electron emission from plasmonic structures

In the previous Chapter we discussed the effect of THz generation from plasmonic structures. The two main mechanisms were proposed to explain the phenomenon, optical rectification in metal surface and electron emission with subsequent electron acceleration in an evanescent plasmonic field. However, neither mechanism was able to explain all the observed effects. In order to find out which phenomena are responsible for the generation of THz radiation from plasmonic structures and to clarify the link between THz generation and electron emission from such structures, we performed a comparison study of both effects on two types of structures, arrays of nanoparticles and of nanoholes.

This Chapter is structured as follows. Firstly, we briefly review the topic of THz generation from plasmonic structures and discuss the proposed mechanisms for explaining the phenomenon. In the second section we report on our experimental results of electron emission and THz generation from two types of samples, and present the numerical modelling of the structures, carried out to calculate the near field enhancement in the vicinity of the metal surfaces. In the third section we discuss the experimental data and compare the phenomena of THz generation and electron emission. We conclude the Chapter by summarizing the results and outlining the plan of possible further investigation into the topic.

5.1 Introduction

In recent years, there have been a number of experiments which have shown THz emission after illumination of metallic surfaces and nanostructures. The first experiments on THz generation by femtosecond laser pulses from optically thin metal films were published in 2004 [91]. Since then different metallic materials and structures have been used to generate THz radiation: thin gold films [92, 149]; nanostructured silver and gold films [94, 150, 151]; semicontinuous metal films [104, 105]; and nanoparticles [105], [152]. Two
distinct mechanisms have been proposed to explain the observed generation of THz radiation in different intensity regimes: optical rectification in metal surfaces [91, 92, 104, 149–152] and electron photoemission [93–95, 105]. In the latter case, THz radiation is produced by the ponderomotive acceleration of the ejected electrons [86] by the high electric field gradients that may occur in the proximity of metal surfaces, owing to plasmonic enhancement [94, 105].

All the reported data can be divided into two groups: those which show only order dependencies not higher than 2 of the THz fluence on the pump power in the whole range of applied pulse energies [104, 149–152], and those which feature of higher than 2 order dependencies [91, 93, 94, 105]. In the second group of measurements the data consist of high-order (3rd – 6th) dependencies of THz fluences at incident intensities below ~10 GW/cm² and low (up to 2nd) order dependencies at incident intensities above ~10 GW/cm². Since optical rectification is a second order nonlinear process, it is, as was mentioned in [93, 94], unable to explain the reported high order dependence of THz fluence on input power. However, the measurements from the first group can be explained by optical rectification due to currents on metal surfaces [150, 151].

To analyse the reported in the literature results further, let us consider the illumination conditions, namely, the applied pump energies. All the reports from the second group state the sample illumination with laser pulses from amplified Ti:sapphire laser with incident intensities in the range of ~1 – 100 GW/cm². The illumination conditions in the first group of reports vary significantly. In the papers [104, 149, 152] non-amplified laser pulses with intensities in the range from 5 to 25 MW/cm² [104] were used, while in reports [150, 151] amplified laser pulses with intensities from 1 to 10 GW/cm² were applied. The results obtained in these two subgroups also vary. In the first subgroup the quadratic dependence of THz intensity on optical power was reported in the whole range of incident intensities used in their experiments without any saturation or transition between the regimes. The reports from the second subgroup show the quadratic dependence at low pump energies, below ~5 GW/cm², with subsequent signal saturation.

As Ramakrishnan et al. recently pointed out [149], the different observed dependencies of the THz fluence on pump power do not necessarily contradict each other, rather they may be associated with different regimes of THz
emission that occur under different experimental conditions. Thus, the results from the first mentioned subgroup are obtained using very low incident intensities, about 2 - 3 orders of magnitude less than those used in the papers which report high order THz fluence dependence [91, 93, 94, 105]. The theory that explains the generation of THz radiation by emission of electrons [93] (see also Chapter 4) predicts the high-order dependence in this region of pulse energies. However, as stated in [149], a low peak-power of laser pulses makes the observation of high-order nonlinearities unlikely. Moreover, the high repetition rate of the used laser source enables lock-in detection that is well-suited for the retrieval of relatively weak signals from second-order nonlinear processes such as optical rectification. Much higher peak power typical for THz generation experiments with amplified Ti:sapphire lasers (in the range of tens of GW/cm² [93]) facilitates the observation of higher-order nonlinear processes.

However, the range of applied pump powers cannot solely determine the dominant mechanism of THz generation. Thus in the second subgroup of the reports which state low orders of THz fluence dependence the used amplified laser pulses had the intensities in the range of units of GW/cm². However, the low-order dependence of THz fluence in these experiments together with the observation of THz radiation from the substrate side of the sample [150, 151] rules out the electron emission mechanism for THz generation.

To find out which mechanisms are responsible for THz generation from plasmonic structures and, in particular, which role the electron emission plays in THz generation, the following experiments are to be carry out. Firstly, comparison study of electron emission and THz generation on the same structures, ideally, under the same experimental conditions needs to be performed. In particular, it is interesting to investigate the dependencies of the electron photoemission current and the intensity of the THz radiation on the incident optical intensity. As discussed in the previous Chapter, both of the effects have similar peculiarities, namely the transitions between the regimes manifested by different orders dependence. Should these transitions happen at the same incident intensities in a comparison study, this would be a strong evidence of the interconnection between the effects.

Secondly, to reveal different phenomena responsible for THz generation, the dependence of THz fluence on optical intensity at the widest possible range of
pulse energies is required. This is especially important for the range of optical intensities below 1 GW/cm^2. This is a challenge because non-amplified pulses with such energy can damage metal structures due to high average pump power [104]; on the other hand, the amplified pulses with energies below 1 GW/cm^2 generate THz signals too weak to be measured in the current set-up. An alternative approach is needed that increases the overall effectiveness of the optical rectification process. The particle arrays used in our previous studies (Chapter 4) are not well-suited for producing optical rectification that can compete effectively with multiphoton photoelectron emission. One reason for this is the low surface coverage of the metal, since the particles occupy only ~8% of the surface area. In addition, the field around such structures is highly concentrated in small areas around the particle tips. To circumvent this problem we investigated an alternative sample design, an array of nanoholes [153, 154]. This triples the fractional coverage of the surface by metal to ~27% yet still retains the advantages of plasmonically enhanced field strengths, albeit that the hole enhancement is ~5 times less than the particle, which is important if higher-order effects are to be seen. Another advantage of this sample design for investigation of low-order effects from such structures is the more uniform near field distribution.

The third approach, which can help to shed light onto the link between THz generation and electron emission from metal surfaces, is a full computer modelling of the latter phenomenon including the calculation of the near field distribution, dynamics of the emitted electrons in plasmon field, and evaluation of the generated radiation due to accelerated movements of electrons. This modelling may explain the observed properties of THz generation, in particular, the dependencies of THz fluence on incident intensity, and show the possible routes to increase the efficiency of the generation mechanism.

In our investigations we pursued the first two approaches. More specifically, we measured the dependence of the THz fluence on the incident intensity over the widest possible range of pump energies and compared the results of THz generation with the electron emission data in similar conditions.

5.2 Experimental results

For a comparative analysis of THz generation and electron emission we fabricated two types of structures: arrays of nanoparticles and nanoholes. The
array of nanoparticles was produced by standard NSL technique; to make the array of nanoholes, the extension of NSL technique was used with etching of polystyrene spheres in oxygen plasma prior to metal deposition (see Chapter 2). To characterize the samples we measured the transmission spectra and compared them with those obtained from FEM modelling (Figure 5.1). For THz generation experiments the samples were fabricated by depositing 50 nm silver layer. For computer modelling, the lateral dimensions of the structures were extracted from SEM images and the metal thickness was taken as 50 nm. For electron emission measurements, another set of samples was fabricated with dimensions close to those used for THz generation. The thickness of the deposited silver layer was 60 nm for nanoparticles and 50 nm for nanoholes.

Figure 5.1. Transmission spectra of the arrays of silver nanoparticles (a) and nanoholes (b). Experimental data are shown in black and the modelled spectra in red. The experimental spectrum in (a) was acquired by microscope spectrometer in TBF mode. The objective used for light collection was Nikon ×40 (NA 0.60, S Plan Fluor ELWD). The experimental spectrum in (b) is obtained by a spectrophotometer. The images in insets represent SEM micrographs of the structures. The scale bar is 2 μm.

Despite the similarities in the fabrication approach, the optical properties of the structures are very different (Figure 5.1). In order to compare the modelling with the experimental data, we measured the transmission spectra of the structures and plotted them together with the calculated transmission spectra in Figure 5.1. The rather complex spectra of nanohole arrays are typical of those obtained from such structures [28], the dip in transmittance at ~700 nm in the data is indicative of the main plasmon resonance associated with the holes. The largest peak at ~850 nm (~1000 nm) in the experimental (modeled) data in the particle array transmission spectrum corresponds to a dipolar plasmon resonance of the particles [133]. The comparison shows that the particle and
the hole resonances are rather well reproduced by the modelling, with a slight shift of the particle resonance wavelength, probably due to absence of the substrate in the model and not full matching the experimental and the modelling geometries.

5.2.1 Electron emission

To find out which role the electron emission plays in the generation of THz radiation, we performed experiments to measure of the electron emission from these structures. The results were obtained from our collaborators in Budapest, from the group of Dr. Péter Dombi, Wigner Research Centre for Physics. The experiments were carried out by István Márton and Péter Rácz. The author greatly appreciates their contribution to the present project.

The electron photoemission after illumination of the samples with femtosecond laser pulses was characterized using a time-of-flight (TOF) spectrometer. The electron emission spectra obtained at different incident intensities are shown in Figure 5.2.

![Figure 5.2](image)

Figure 5.2. Electron emission spectra as a function of optical intensity for arrays of nanoparticles (a) and nanoholes (b).

The spectra show the generation of high-energy electrons with kinetic energy up to 60 eV which is much higher than that of the photons in the laser pulse (1.55 eV). This indicates that the emitted electrons are accelerated by enhanced plasmon fields in the vicinity of the metal surfaces. The observed spectral features are similar to those obtained in electron photoemission experiments on other types of metal nanostructure [88].

The cutoff energy taken at the level 0.01 of electron spectral density is plotted in Figure 5.3a. From the data it is seen that the cutoff energy scales approximately.
linearly with incident intensity. This indicates a ponderomotive character for the electron acceleration, since the ponderomotive potential linearly depends on incident intensity, see Eq. (4.5).

Figure 5.3. Electron emission data. (a) Cutoff energies at the level of 0.01 of electron spectral density versus incident intensity for nanoparticles (black) and nanoholes (red). The solid lines are linear fits to the data. (b) Electron emission photocurrent as a function of optical incident intensity for arrays of nanoparticles (black) and nanoholes (red) made by NSL technique. The numbers in the brackets are the fitted orders of the processes.

The integrated photocurrent as a function of incident intensity is shown in Figure 5.3b. The power function is used to fit the experimental data. The numbers near to the curves indicate the effective order of the processes. There are two different regimes of the electron emission which contribute to the overall photocurrent. At low incident intensity, the electrons are liberated via multiphoton photoemission, which turns into tunnel photoemission at higher intensities [142]. The first regime manifests itself by a high-order dependence of photocurrent on pulse energy. The order of the process corresponds to a number of photons required to liberate a single electron. Since the photon energy in our experiment is about 1.55 eV and the silver work function is 4.1–4.7 eV [145, 146], 3 to 4 photons are required to liberate one electron. The experimental data are in good agreement with this simple approach. At the intensity above the transition point, at the regime of tunnel ionization, the experimental data show a lower-order dependence. This is because in this regime the electrons tunnel through a tilted vacuum potential so that less energy, and thus fewer incident photons, are required. The experimental data are also in good agreement with previously published results on electron emission from silver films [142, 155].
It is worth to note that because the plasmon field distribution in the vicinity of the metal surface is highly inhomogeneous and thus the near field enhancement strongly varies in space, both mechanisms, multiphoton and tunnel photoemission, contribute to electron emission both below and above the transition intensity. However, the relative weights of these contributions depend on incident intensity, which allows to differentiate these processes at the intensities far from transition point. The detailed analysis of both mechanisms in overall photocurrent from nanoparticles at different incident intensities can be found in recent paper by P. Dombi et al. [88].

5.2.2 THz generation

We measured THz fluences from arrays of both structures as a function of incident intensity in the range over nearly three orders of magnitude, from 0.3 to 200 GW/cm² (Figure 5.4a). The spectra of the emitted THz pulses are obtained by Fourier transform of the time-domain signal from nanoparticles and nanoholes at incident intensity ~ 20 GW/cm² are shown in Figure 5.4b. The intensity dependence data, obtained for arrays of nanoparticles, exhibits two main regions in agreement with previously published results on THz generation from metal structures [91, 93, 94, 105]. For incident intensities below 10 GW/cm² the data show a 4.7 effective order of the process, indicative of multiphoton electron photoemission. For incident intensities above 10 GW/cm² the data show a much reduced power dependence, which can be ascribed to tunnel ionization. For the lowest pump intensities for which we were able to collect useful data there is no sign of a transition to the lower-order dependence we expect for optical rectification.

In contrast, the data from the nanohole arrays show three different regions. For intermediate incident intensities, between ~5 GW cm⁻² and ~50 GW cm⁻², the data show a 3.7 order dependence of the THz fluence on the incident optical intensity. This is similar to our results for particles, for which we observed a 4.7 order dependence. Again, these higher-order dependencies are indicative of multiphoton photoelectron emission [105]. Above ~50 GW/cm², the THz fluence starts to saturate in a way that is similar to that which we observed for particles. However, the new aspect revealed in these data from hole arrays concerns the low intensity regime, for incident intensities below ~5 GW/cm² the data show a transition to a less than second-order dependence. Such a low order...
dependence is not consistent with multiphoton electron photoemission mechanism, since according to the model of THz generation discussed in Chapter 4, in the intensity range below \( I_{\text{opt}}^{\text{pon}} \) a transition to higher order dependence is expected.

![Figure 5.4](image)

**Figure 5.4.** THz emission data. (a) THz fluence as a function of optical incident intensity for arrays of nanoparticles (black) and nanoholes (red) made by NSL technique. The numbers in the brackets are the fitted orders of the appropriate sections of the data. (b) The normalized spectra of the emitted THz radiation for nanoparticles (black) and nanoholes (red) at incident intensity \( \sim 20 \text{ GW/cm}^2 \).

To estimate the transition intensity value \( I_{\text{opt}}^{\text{pon}} \), we make use of the relation (4.7).

While both \( I_{\text{opt}}^{\text{mpe}} \) and \( I_{\text{opt}}^{\text{pon}} \) depend on the field enhancement factor, their ratio does not include any information on the value of the local fields. Taking into account the plasmon decay length for nanoholes is of the same order as for nanoparticles [156], \( \alpha \sim 10\text{–}20 \text{ nm} \), we may estimate the ratio \( I_{\text{opt}}^{\text{mpe}} / I_{\text{opt}}^{\text{pon}} \) for nanoholes to be the same as for nanoparticles. For nanoparticles, this ratio was found to be 8 (see section 4.6). Since for nanoholes the transition intensity between the regimes of multiphoton and tunnel photoemission is \( I_{\text{opt}}^{\text{mpe}} = 50 \text{ GW/cm}^2 \) (Figure 5.4a), the value of \( I_{\text{opt}}^{\text{pon}} \) is estimated to be \( \sim 5 \text{ GW/cm}^2 \). Thus, if the electron emission is supposed to be the only mechanism of THz generation, then for optical intensities below \( \sim 5 \text{ GW/cm}^2 \) one should expect a transition to a higher-order dependence. Contrary to this prediction, the THz fluence dependence in this region of optical intensities undergoes a transition to a lower-order dependence. Moreover, the observed order of the process is inconsistent with a multiphoton photoemission mechanism. This contradiction between the model prediction and the experimental data suggest that there may be another mechanism responsible for THz generation in this
range of optical intensities. We propose that optical rectification is a possible mechanism in this region of incident intensities. Indeed, the order of the dependence rules out the electron emission as a mechanism for THz generation. Moreover, at this region the low pulse energies may be not sufficient to generate THz radiation through electron emission, and another nonlinear process of a lower order may become dominant.

In addition to above data analysis, another observation indicates a shift between the mechanisms of THz generation with a transition at an incident intensity of 5 GW/cm². The shape of the time-domain signal changes when the incident intensity increases above this value (Figure 5.5a). In conjunction there is also a change in the spectrum of the THz radiation (Figure 5.5b), namely a second peak appears at higher frequency. This observation is specific to nanohole array; for nanoparticle array the THz pulse spectrum and the shape of the time-domain signal varies only slightly over the whole range of incident intensities used in the experiment.

Figure 5.5. THz data taken from the nanohole array at incident intensities of 4.4 GW/cm² (black) and 8.0 GW/cm² (red). The time-domain signals are shown in (a), and the spectra of THz pulses are shown in (b). Small oscillations in the spectra at frequencies above 0.5 THz are probably due to noise in the time-domain signal.

To investigate this effect in detail we plotted the time-domain signals and the THz radiation spectra for a range of incident intensities from 4.4 GW/cm² to 64.2 GW/cm² (Figure 5.6). From the data shown in Figure 5.6a it can be seen that the signal shape abruptly changes when the intensity is increased from 4.4 GW/cm² to 8.0 GW/cm². In particular, the second minimum (negative peak) becomes much more distinctive. With further increase in incident intensity, the shape of the signal continues to change, but much more gradually. The ratio of
the magnitude of the main (positive) and second (negative) peaks changes with a higher amplitude of the positive peak at low incident intensities turning into a higher amplitude of the negative peak at higher pump energies. The continuous transformation of the time-domain signal with incident intensity leads to signals at the lowest (4.4 GW/cm²) and the highest (64.2 GW/cm²) intensities looking as though they have reversed phases (all the parameters of lock-in detection were the same during the data acquisition). To show this effect more clearly, we plotted these normalized signals on one plot with a reversed phase for the second signal (Figure 5.7a).

![Figure 5.6](image.png)

Figure 5.6. Evolution of (a) time- and (b) frequency-domain signals acquired from the nanohole array at incident intensities of (4.4, 8.0, 18.2, 23.9, 37.6 and 64.2) GW/cm². The signals are normalized and upshifted for comparison’s sake.

On increasing the incident intensity the THz spectra also change. The spectrum abruptly changes when the intensity increases from 4.4 GW/cm² to 8.0 GW/cm², namely, the spectral maxima shift from 0.4 THz at lower intensity to 0.65 THz at higher pulse energies. With a further increase of the pump power both maxima in the spectrum develop, giving a single peak at moderate incident intensities, 20 – 40 GW/cm². At the highest intensity (64.2 GW/cm²) these two peaks (occurring at frequencies 0.4 and 0.65 THz) appear distinct again. The frequency peaks coincide with those obtained at intensities 4.4 GW/cm² and 8.0 GW/cm² (Figure 5.7b).
Such signal and spectral evolution, with an abrupt change at the incident intensity where the transition between the order dependence occurs, most probably indicates a shift between different regimes of THz generation. However, further investigation of this effect is required to understand these phenomena better.

![THz emission data](image)

**Figure 5.7.** THz emission data taken from the nanohole array. (a) Time-domain signal obtained at incident intensities of 4.4 GW/cm$^2$ (black) and 64.2 GW/cm$^2$ (red). (b) Spectra of THz pulses generated at incident intensities of 4.4 GW/cm$^2$ (black), 8.0 GW/cm$^2$ (blue) and 64.2 GW/cm$^2$ (red). The data are normalized and the phase of the signal in (a) taken at intensity of 64.2 GW/cm$^2$ is reversed.

### 5.2.3 Computer modelling

For THz generation and electron emission process from plasmonic structures the crucial parameter is the strength of the electromagnetic field in the vicinity of the metal surface. To investigate the distribution of near fields, the finite element modelling (FEM) of the structures was carried out (Figure 5.8). The results from computer modelling were obtained by Dr. Euan Hendry, the author is indebted to him.

In Figure 5.8 we show the calculated field distributions associated with the plasmon modes supported by the nanoparticle and nanohole structures, calculated at the frequency of the particle plasmon resonance, 300 THz. From these data we see that the maximum field enhancement for particles and holes differ by a factor of ~ 5. The field enhancement for hole arrays is ~ 2 - 3 whilst that for particles is ~ 10 – 15. What consequences will this change in the field enhancement cause? Firstly, it will reduce the THz generation efficiency, and in particular, may reveal other mechanisms of THz generation at low incident intensity which may be hidden in structures with stronger enhancement factors. Secondly, as it follows from the model proposed in Chapter 4, the transition
between the regimes of multiphoton photoemission and tunnel ionization is inversely proportional to the square of the enhancement parameter, see the relation (4.4). Thus the transition intensities for the two structures should differ by at least an order of magnitude, which is consistent with our measurements, see Figure 5.4a.

Figure 5.8. Field distribution around a) particles and b) holes calculated using finite element modelling. Incident light with a wavelength of 1000 nm is normally incident on the substrates. The plots show time-averaged magnitude of the electric fields. The solid lines outline the metal structure edges.

5.3 Discussion of the results

In order to compare the data obtained for electron emission and THz generation, we will discuss them together (see Figure 5.3b and Figure 5.4a). Both sets of data contain similar regions. For nanoparticles, there are regimes with high-order dependence at low incident intensity, which turns into a low-order dependence at higher intensities with the transition point at about 10 GW/cm² for THz and 30 GW/cm² for electron emission data. The THz and electron emission signal for nanoholes contain similar regions with transition intensity at very similar values, 50 GW/cm² for THz and 60 GW/cm² for electron emission data. In addition, THz emission data for nanoholes contain a region with a low-order dependence, which can be attributed to some other nonlinear mechanisms rather than electron emission. In this region of intensity we should expect an extremely low photocurrent, so that these unknown mechanisms can reveal themselves. Unfortunately, the available equipment does not allow us to acquire reliable data in this region of intensities. Nevertheless, the electron emission spectrum at the lowest energy used in experiments (see Figure 5.2b) shows extremely small energies of the emitted electrons which confirms the supposition that THz radiation in this region of intensities could not rely on the emission of electrons. The most probable candidate for THz generation mechanism at low incident intensity is optical rectification [149], which is...
manifested by a nearly second-order dependence of THz fluence on incident intensity. Though there are some similarities in both data sets, there is no full match between them. Thus, the transition points between the regimes of multiphoton photoemission and tunnel ionization in THz radiation and electron emission data for particles differ by a factor of 3. This cannot be ascribed to a systematic error in estimation of the incident intensity, since the transition points between the regimes for nanoholes in THz generation and electron emission data nearly match each other. Another discrepancy between both sets of data is the relative magnitudes of the THz radiation intensity and the electron emission current for nanoparticles and nanoholes. The latter observation can be accounted for by a qualitative description of the THz radiation mechanism based on the emission and acceleration of electrons which seems to be the dominant effect at these high incident intensities. According to this approach (see Chapter 4) it is expected that the emitted THz electric field strength is proportional to the product of the number of the emitted photoelectrons $N$ (photocurrent) and their acceleration $a$, see the relation 4.2.

The electron emission current is higher for nanoparticles (Figure 5.3b), since the peak field-enhancement around the nanoparticles is higher than that for nanoholes. However, the energy gained by electrons liberated from the metal surface of nanoholes is higher than that from nanoparticles at incident intensities above $\sim 50$ GW/cm$^2$ (Figure 5.3a). Higher energies gained by electrons mean higher average electron acceleration. This is probably due to peculiarities of the field distribution around the metal structures. From FEM modelling (Figure 5.8) it follows that the highly enhanced near field around nanoparticles is concentrated in small areas near to particle tips. In contrast to that, the field around nanoholes is more uniform though having lower peak enhancements. The higher electron acceleration from nanoholes together with the saturation of the photocurrent from nanoparticles at incident intensities above 30 GW/cm$^2$ leads to a stronger THz field generated by nanoholes at high pump powers.
5.4 Summary and conclusions

In this work we tried to untangle the situation with THz generation from plasmonic structures. Since the first experimental observation of the THz generation from optically thin metal films [91], two main mechanisms were proposed to explain the THz generation from such structures, optical rectification and electron emission, supported by different dependencies of THz fluence on pump power. Recently, it has been suggested [149] that the different observed dependencies do not necessarily contradict each other, but rather they may be associated with different regimes of THz emission that occur under different illumination conditions. In our work we sought to investigate samples that would show THz emission arising from both optical rectification and electron photoemission. We corroborated the THz generation results by electron emission measurements. To the best of our knowledge these are the first results to directly compare the phenomena of THz generation and electron emission from similar sets of samples.

Our THz generation data from metallic nanohole arrays, Figure 5.4a, show that the THz fluence from the structure illuminated by femtosecond laser pulses has an incident intensity dependence that provides evidence for two generation mechanisms. At lower incident intensities, below 5 GW/cm², the THz fluence has a ~1.5 order dependence on the incident optical intensity. For incident optical intensities above 5 GW/cm² a higher-order dependence is observed, consistent with electron emission mechanism of THz generation. It was also shown that THz signal and its spectrum change when incident intensity passes through a transition point, indicating a further change in the generation mechanism.

In addition, our electron emission measurements support this two-mechanism model, though we were not able to obtain reliable electron emission data at incident intensities where we expect optical rectification to be the dominant mechanism. However, the low energy of the emitted electrons at this range of incident intensities indicates that THz generation at low pump powers cannot be due to the emission of electrons. Similar behaviour of the intensity dependencies of the THz generation and electron emission data at high pump powers confirms that the generation of THz radiation in this range of pulse energies from the investigated samples is a result of the electron emission.
THz generation and electron emission from plasmonic structures

The two-mechanism model of THz generation in different range of incident intensity can explain most of the published results on THz generation from plasmonic structures. According to this approach, in the reports containing high order dependence data [91, 93, 94, 105] the dominant mechanism is the electron photoemission, with multiphoton photoemission at low pulse energies where the high-order dependence of THz fluence is observed, and tunnel photoemission at higher pump powers where the signal saturation is observed. In the experiments that demonstrate only low-order dependencies of THz fluence [104, 149–152] the most probable mechanism is optical rectification on metal surfaces. While the low pump energies used in the experiments [104, 149, 152] make the THz generation to be unlikely based on the electron emission in these experiments, reports [150, 151] state the high energy of used pump pulses, of the order of several GW/cm^2, the range where the electron emission from plasmonic structures is expected to be the dominant mechanism for THz generation. However, the low-order dependence of THz fluence together with the observation of THz radiation from the substrate side of the sample rules out the electron emission as a mechanism for THz generation in these experiments. The plausible explanation for the results could be the low efficiency of electron emission from the structures used in the experiments due to low near field enhancement. However, to finally settle this issue a further investigation is required.

To gain further insight the phenomenon of THz generation from plasmonic structures one has to conduct a full FDTD modelling of the structures calculating the near field distributions in the vicinity of the metal surfaces and simulating the dynamics of the emitted electrons. Such an analysis has been carried out in the recent paper by P. Dombi [88]. Solving for the electron dynamics allows one to evaluate the characteristics of THz radiation due to the accelerated movement of electrons. This can help us to understand better the reasons for the discrepancy between the measured and predicted order of the THz fluence dependence at different pump powers, and to specify the intensity range in which THz generation occurs via photoelectron emission.
Chapter 6
Temperature and pressure effects in THz generation from plasmonic structures

In this Chapter we report on our investigations of optically-induced THz generation from plasmonic structures as a function of temperature and pressure. As was shown in Chapter 4, THz generation from plasmonic structures crucially depends on the electromagnetic field enhancement, due to its high-order dependence on the incident optical intensity. We investigated the temperature dependence of THz generation efficiency for a number of semicontinuous silver films over a range of temperatures from 300 K down to 10 K. The maximum values of the THz intensity enhancement at low temperatures strongly vary from sample to sample with the strongest observed intensity enhancement of about 2 orders of magnitude. We suggest this effect is most likely due to a reduction in ohmic losses due to suppressed electron-phonon scattering.

6.1 Temperature effects

The field of plasmonics relies on the collective oscillations of free electrons in metals. All plasmonic-related effects suffer from strong damping of the electron oscillation, which is an intrinsic property of normal metals. The effects of plasmonic sensing [157], plasmon-assisted electron emission [158], SERS [140], metal-enhanced fluorescence [159] and others would all benefit from a reduction of the intrinsic losses in the metal [160]. In recent years great efforts were made to overcome the losses in plasmonics. One of the ways to alleviate SPP damping is through the use of gain media [161].

Whilst investigations in coupling of plasmonics and gain media shows great potential, another route to suppress electron oscillation damping, namely low temperatures, has arguably received less attention. Only recently the effects of low temperatures in plasmonics have been investigated [11, 162–164] demonstrating the advantages of such an approach. In this section we describe our investigation of the effect of the temperature on metal losses by using the phenomenon of THz generation from plasmonic structures.
6.1.1 Temperature dependence of metal losses

The plasmon damping in noble metal structures originates from the electron-electron and electron-phonon scattering in the bulk metal. Besides that, in the nanoparticles there are two extra channels for energy dissipation, radiative losses and electron-surface scattering. Thus the particle plasmon resonance damping rate is the sum of all these four contributions [11]

$$\gamma = \hbar \left( \frac{1}{\tau_{e-e}} + \frac{1}{\tau_{e-p}} + \frac{1}{\tau_{r}} + \frac{1}{\tau_{e-s}} \right).$$  \hspace{1cm} (6.1)

The electron-electron relaxation time \(\tau_{e-e}\) was investigated in [165–167] and is given by the expression

$$\tau_{e-e}^{-1}(T) = \frac{\pi^3 \Gamma \Delta}{12 h E_F} \left[ (k_B T)^2 + (h \omega / 2 \pi)^2 \right],$$ \hspace{1cm} (6.2)

where \(E_F\) is the Fermi level energy, \(\omega\) is the angular frequency of the incident light, \(\Gamma\) is the Fermi-surface average of the scattering probability, and \(\Delta\) is the fractional umklapp scattering probability. For the range of temperatures used in our experiments the first term in the square brackets in the expression (6.2) is much lower than the second one and thus the temperature dependence of the electron-electron scattering is negligible.

The electron-phonon scattering time \(\tau_{e-p}\), derived in [168–170], is given by

$$\tau_{e-p}^{-1}(T) = \tau_0^{-1} \left[ \frac{2}{5} + 4 \left( \frac{T}{\Theta} \right)^5 \int_0^{\Theta / T} \frac{z^4}{e^z - 1} \, dz \right],$$ \hspace{1cm} (6.3)

where \(\tau_0\) is material-dependent constant and \(\Theta\) is the Debye temperature. The temperature dependence of the bulk electron relaxation rate, the sum of the electron-electron and electron-phonon scattering rates, for silver and gold is plotted in Figure 6.1. The relaxation rate is a nearly linearly decreasing function of temperature in the range 300 – 100 K with a saturation below 50 K.

The contributions to the energy dissipation from the radiative losses and electron-surface scattering are found to be temperature independent [11]. Thus, the main contribution in the temperature dependence of the plasmon resonance damping is the electron-phonon scattering. The experimentally measured electron relaxation time for gold nanoparticles over the range of temperatures 293 – 6 K shows a 30% reduction in the plasmon damping [11]. In that paper it was shown that the temperature dependence of the electron relaxation rate is in
good agreement with the theory. It is interesting to note that since the electron-electron and electron-surface scattering, and radiation losses are temperature independent, they give rise to an offset in the plasmon damping dependence. Thus, the higher these losses, the less damping reduction could be achieved with a temperature decrease. The electron-electron scattering is expected to be smaller in silver as compared to gold [11] and thus a higher extent of plasmon damping reduction for silver particles could be achieved.

Figure 6.1. Temperature dependence of the bulk electron relaxation rate for silver (black) and gold (red).

6.1.2 THz generation efficiency as a function of temperature

In Chapter 1 we showed that the field enhancement in the vicinity of the metal structures near the plasmon resonance is nearly inversely proportional to the plasmon damping rate (see Eq.(1.68)). Thus, a suppression of the metal intrinsic losses increases the particle field enhancement. In addition, in Chapter 4 it was demonstrated that the THz intensity generated from plasmonic structures strongly depends on the electric field enhancement. We have shown that in the low range of incident intensities a high-order dependence of the THz fluence on the pump power is obtained which leads to a strong sensitivity of the THz intensity to the changes in the electromagnetic field enhancement. For instance, a $5^{th}$ order dependence of the THz fluence gives $10^{th}$ power dependence of the THz intensity on the field enhancement factor. Thus, only a two-fold increase of the near field, results in about 3 orders of magnitude enhancement of the THz generation efficiency.
Temperature and pressure effects in THz generation from plasmonic structures

To investigate the effect of temperature on THz generation efficiency we used a conventional THz spectrometer (see Chapter 2) with the sample being placed in a cryostat. The effect was investigated in the temperature range 300 – 10 K for semicontinuous films made of silver and gold. The representative dependences of the THz radiation intensity as a function of temperature are shown in Figure 6.2 for silver and Figure 6.3 for gold. The qualitative behaviour of the dependence for the THz intensity resembles an inverted dependence for the relaxation rate (Figure 6.1). For silver films the THz intensity nearly linearly depends on the temperature over the temperature range between 300 and 100 K and saturates below 50K (Figure 6.2). For gold films the THz intensity seems to depend nearly linear on the temperature without a saturation at low temperatures (Figure 6.3).

Figure 6.2. Temperature dependence of the THz intensity obtained from two different spots on the same semicontinuous silver film. The THz intensity is normalised to its value at room temperature.

The parameter which determines the temperature dependence of the plasmon decay rate and thus the near field enhancement for different materials is the Debye temperature. The Debye temperatures of silver and gold are quite similar, 225 and 165 K, respectively [171]. The smaller Debye temperature of gold leads to a slightly lower saturation temperature (Figure 6.1). We assume that it is the lower Debye temperature of gold which leads to a difference in the temperature dependence for these two metals at low temperatures. The similarity between the temperature dependences of the plasmon decay rate and the THz intensity confirms the role of the reduction in the electron-phonon scattering for the observed phenomenon.

The THz intensities in Figure 6.2 and Figure 6.3 are normalised to the THz intensity at room temperature and thus the numbers along the intensity axis
give an absolute value of the THz generation efficiency enhancement. The data shown in panels (a) and (b) of the Figure 6.2 were obtained from the same sample at two different positions. Whilst the data acquired from the same spot in the sample show good repeatability, the maximum THz intensity enhancement strongly varies between different spots in the sample. Similar results were obtained for gold films, see Figure 6.3. In our measurements we were not able to find any correlation between the sample thickness or its morphology and the THz intensity enhancement. However, there is a correlation between the THz intensity signal at room temperature and the intensity enhancement at low temperature. Normally, THz signals which are strongly enhanced at low temperature are weak at room temperature.

![Figure 6.3. Temperature dependence of THz intensity obtained from two different semicontinuous gold films. The THz intensity is normalised to its intensity value at room temperature.](image)

The time-domain and frequency-domain signals of the data shown in Figure 6.2b are plotted in Figure 6.4 for the temperature range from 290 to 20 K. With decreasing temperature, the signal increases without a significant change in its shape. We observed a similar behaviour when the intensity dependence of the THz fluence was investigated. This behaviour is expected since the strength of the near field is a product of the strength of the incident light field and the field enhancement factor, so that these two values are interchangeable.

While the temperature dependence of the emitted THz intensity and its strong enhancement at cryogenic temperatures are expected and could be well understood in the framework of the theoretical considerations provided above, some results could not be easily explained with this simple model. For example, the different enhancement ratios were obtained from different samples. The model predicts that the narrowing of the plasmon resonance and thus the THz
Temperature and pressure effects in THz generation from plasmonic structures

intensity enhancement depend only on the material constants of the metal. However, the experimental data show intensity enhancement values which differ by orders of magnitude, even for the same sample (Figure 6.2). Another puzzling observation is the different THz intensity temperature dependences, one of them is shown in Figure 6.6b.

Figure 6.4. Time-domain (a) and frequency-domain (b) signal from the semicontinuous silver film (Figure 6.2a). The data are shown for the temperatures 290, 260, 220, 180, 140, 100, 50, and 20 K. The arrow indicates the direction of the temperature increase.

To explain the first result one needs to take into account the fact that the ratio of the reduction of the plasmon resonance decay rate depends not only on the metal constants but also on the values of the radiative damping and electron-surface scattering both of which vary with the particle geometry. The semicontinuous metal films provide a diverse range of the sizes and shapes of the structures where the plasmon resonances occur [116], which can result in different values of radiative damping and electron-surface scattering. This can cause different temperature dependences obtained at different spots on the sample surface.

The second result can be explained by recalling that the increase in the field enhancement with narrowing of the plasmon resonance depends on the relative positions of the plasmon resonance and the pump pulse frequency. Thus, if the structure is pumped at its plasmon resonance frequency, then the strong field enhancement could be achieved with resonance narrowing. Otherwise, the field enhancement might in fact decrease due to resonance narrowing. In addition, we note that a slight change in size and shape of the metal clusters due to thermal expansion or contraction might also cause a shift in the resonance position [172, 173].
6.1.3 Temperature dependence of the order of the THz generation process

Figure 6.5. Intensity dependence of the THz radiation fluence at different temperatures and pressures. The experimental conditions are shown in the figures. The numbers in brackets are the fitted orders of the processes.

To investigate further the temperature effects in THz generation from plasmonic structures we performed experiments by measuring the intensity dependence of the THz fluence at different temperatures from semicontinuous silver films. The experiments revealed a change in the order of the process with temperature. Thus, we found that the THz fluence dependence measured in the cryostat at low temperature (10 K) and pressure (10^-5 mbar) have the order dependence \( n = 3.9 \), which is lower than the order of the process that was previously measured from such structures (see section 4.5). The measurements of the order dependence from the same sample outside the cryostat at normal temperature (290 K) and pressure (1 atm) show the expected value of the THz fluence dependence, \( n = 5.0 \) (Figure 6.5a). However, there were some changes, other than temperature, in the experimental conditions, which could, in principle, affect the order dependence. Thus, to measure the THz fluence dependence at low temperature, the sample was placed in cryostat, then the chamber was pumped down and then temperature was decreased. We found
Temperature and pressure effects in THz generation from plasmonic structures that the measured THz fluence changes at each of these steps. Firstly, the cryostat reduces the measured THz signal due to a spatial clipping of the radiation by cryostat windows. This also affects the shape of the THz pulse and its spectrum. In addition, the quartz windows of the cryostat absorb some of the THz radiation. On the second step, during pumping down the cryostat chamber, the THz intensity increases. The investigation of this effect is reported in the next section. On the last step, at the temperature decrease, the THz intensity normally increases.

We do not expect the change in the order of THz fluence dependence after the first two steps, however, to check this we performed measurements of the effective orders of the process at low incident intensities range at each of these steps. We found that indeed after placing the sample in cryostat (Figure 6.5b) and pumping down the chamber (Figure 6.5c) no changes in the order of the process were observed. However, the cooling down results in the order dependence change, see Figure 6.5d. By decreasing the temperature from 290 K to 10 K the THz fluence intensity dependence drops from 5.0 to 3.9, see Figure 6.5d.

Figure 6.6. Intensity dependence of the THz fluence at different temperatures and pressures (a). Temperature dependence of THz fluence at different incident intensities, 9.1 GW/cm\(^2\) (b) and 2.7 GW/cm\(^2\) (c). The THz intensity is normalised to its value at room temperature.

In Chapters 4 and 5 we showed that THz generation from semicontinuous metal films could be assessed in the context of a model based on electron emission. To be liberated from a metal, an electron has to overcome the corresponding work function. Since the incident photon energy (1.55 eV) in our experiments is
lower than the value of silver work function, in the low range of incidence intensities (1 – 10 GW/cm²) the electrons are emitted via a multiphoton photoemission process [142]. In this regime of electron emission several photons to be absorbed to liberate a single electron. This manifests in high order dependence of the emission photocurrent on incident intensity. Such steep dependence can explain a high order dependence of the THz fluence on pump power. 

Thus the change in the order of the THz fluence dependence at low temperature should indicate a change in the work function of the metal. It is known that the work function of most metals slightly depends on the temperature [174]. The temperature coefficient of silver work function is negative \( k_s = -1.34 \times 10^{-4} \text{ eV/K} \). This means that the work function decreases with temperature. This should lead to a higher order dependence in THz fluence dependence at low temperatures which contradicts our observations. Moreover, such a weak temperature dependence at the temperature difference of ~ 300 K would change the work function only by \( \Delta \varphi = k_s \Delta T \approx 0.04 \text{ eV} \) and thus the THz fluence order dependence would change by \( \Delta n_{\text{exp}} = 2\Delta \varphi / 1.55 \text{ eV} \approx 0.05 \). This is much lower than the observed value \( \Delta n_{\text{exp}} = 5.0 - 3.9 = 1.1 \). This implies that there is another mechanism which determines the change in the order dependence. To address this problem, further investigations are required. It would be necessary to investigate the temperature dependence of electron emission order dependence on incident intensity in order to see if there are correlations between the temperature dependences in both phenomena.

While there is no clear explanation for the THz generation order change with temperature, the effect can explain the observed complex temperature dependences of the THz intensity in some experiments (Figure 6.6b). Figure 6.6 shows two types of THz intensity temperature dependences, monotonic dependence (Figure 6.6c) and non-monotonic one (Figure 6.6b). The monotonic dependence resembles those shown before for both silver and gold and is expected from the theory; the non-monotonic dependence could not be explained simply by a reduction in the plasmon damping at low temperatures. However, since the THz fluence effective order changes with temperature, the THz intensity temperature dependences measured at different incident intensities could perhaps be of different forms as shown in Figure 6.6.
Temperature and pressure effects in THz generation from plasmonic structures

6.1.4 Pressure effects

In the electron emission model of the THz generation a question arises as to whether electrons ejected from the metal can propagate far enough for them to produce the currents responsible for the THz emission, since the electron propagation will be limited by scattering from air molecules. Ejected electrons need to be able to travel distances in air of the order of ~20 nm normal to the sample surface without being scattered. This is the length scale of the field localization around the nanoparticles (see Chapter 4). The strongest scattering of electrons with energies in the range 0.1 - 100 eV in air will be due to nitrogen molecules. The maximum scattering cross-section in this energy range is \( \sigma_{\text{sca}}^{N_2} \approx 3 \times 10^{-20} \text{ m}^2 \) [175]. The density of air molecules at standard temperature and pressure is \( n \approx 3 \times 10^{25} \text{ m}^3 \), thus the mean free path is

\[
I = \frac{1}{\sqrt{2\sigma_{\text{sca}} n}} \approx 80 \text{ nm.} \tag{6.4}
\]

![Figure 6.7. Pressure dependence of the THz generation efficiency from silver (a) and gold (b) semicontinuous films. The THz intensity is normalised to its value at normal pressure. Inset of the panel (a): schematic dependence of the electron mean free path as a function of the air molecules concentration or air pressure. Inset of the panel (b): schematic dependence of the electron beam transmission in air in semilogarithmic coordinates (the pressure axis is in logarithmic scale).](image)

To find out whether electron scattering on air molecules plays a significant role in THz generation, we measured the THz intensity generated from semicontinuous silver and gold films as a function of air pressure in the range from the normal atmospheric pressure down to \( 10^{-6} \text{ mbar} \). Representative plots of the THz intensity vs pressure are shown in Figure 6.7. The experimental results suggest that the THz intensity abruptly increases at a pressure below 1
The THz intensity is normalised to its value at normal pressure and thus the values in the vertical axis are calibrated in terms of the absolute intensity enhancement. We also measured the generated spectra of the THz pulses. The shape of the time-domain and frequency-domain signals taken at normal and at low pressure show no detectable difference.

Let us now discuss the pressure dependence we should expect in the case where the liberated from metal electrons are scattered by air molecules. There should be a concentration $n_0$ above which the electron scattering will affect the measured intensity. The inset of Figure 6.7a depicts a schematic plot of the electron mean free path in air as a function of air pressure or the air molecule concentration. The pressure and the concentration with index “0” correspond to a mean free path which is comparable to the characteristic length of the electron propagation $l_0 = 20 \text{ nm}$. In this simple consideration we do not aim to find an exact solution of the effect of the air molecules on the THz generation but rather we try to understand the main features of the experimental results. The strength of the generated THz electric field is proportional to a number of the emitted electrons (see Chapter 4) and thus the scattering of the generated electrons by air molecules will reduce the generation efficiency. To find how the transmission of electrons depends on the air pressure we make use of the Beer-Lambert law, which is applicable for non-interaction low energetic electrons

$$T = \exp(-l_0/l) = \exp(-P/P_0).$$

The dependence (6.5) is plotted in semilogarithmic coordinates in the inset of Figure 6.7b. As expected, the transmissivity abruptly changes at the transition pressure $P_0$ at which $l = l_0$. The dependences of the measured THz intensity and the electron transmission as a function of pressure have similar features: weak dependence at the pressure range $P \ll P_0$ and $P \gg P_0$ with a strong dependence around $P_0$. From the experimental data shown in Figure 6.7 it follows that the transition pressure lies in the range $1 - 10 \text{ mbar}$ which is $2 - 3$ orders of magnitude smaller than what we have estimated from the electron scattering cross-section values given above. Partly this mismatch could be attributed to complex trajectories of electrons during the acceleration by ponderomotive forces [176]. However, such a huge mismatch between the
Temperature and pressure effects in THz generation from plasmonic structures. Experimental data and the simple model prediction might be an indication of different mechanisms for the THz intensity enhancement at low pressures. One possible reason could be the presence of surface contamination affecting the generation efficiency. The most probable candidate for this role is the thin water layer which is always present on top of nanostructures in ambient atmosphere [177]. This layer may be partly evaporated at low pressures which would lead to a smaller electron absorption in the water layer and a higher generation efficiency. However, if the observed pressure dependence were indeed due to a water layer, then it would be much smoother than the measured one.

6.2 Summary and conclusions

In conclusion, we have measured the temperature dependence of the emitted THz radiation from semicontinuous silver and gold films in the temperature range 300 – 10 K and discovered a strong dependence of the generation efficiency on sample temperature. We ascribe this effect to a reduction of the SPP damping, which is due to the suppression of the electron-phonon scattering at low temperatures. The strong temperature dependence of the emitted THz intensity most likely results from the high order (~5th) of the generation mechanism.

The reported THz emission measurements could be utilized for sensitive investigations of low-temperature plasmonic effects. Moreover, we note that such sensitivity of the THz generation to the changes in the imaginary part of the metal dielectric constant makes the effect suitable for the investigation of SPP damping mechanisms as well as the interaction plasmonic structures with gain media.

In addition, measurements on the intensity dependence of the THz fluence at low temperatures reveal a change in the effective order of the process with temperature. While the interpretation of the effect seems complicated, the observed change of the order dependence explains the more complex temperature dependences than those predicted by the provided theory.

We also measured the pressure dependence of the THz intensity. The results are assessed by the absorption of the emitted electrons in air. While this approach explains the main features of the pressure dependence, an estimate of the transition pressure does not agree with the experimental value. This
mismatch can perhaps be partly explained by complex electron trajectories during the electron acceleration in oscillating electric and magnetic fields. However, to better understand the observed temperature and pressure dependences considerable further work is required.
In this Chapter we report on our measurements of selective THz frequency generation via irradiation of microstructured semicontinuous silver films using femtosecond laser pulses and compare the results with those obtained from analogous unstructured sample. A simple analytical model based on the field distribution for an array of THz dipole emitters is used to interpret the experimental data and to explain the main features of the generated radiation patterns, including the resonances in the emission spectrum.

7.1 Introduction

As was shown in Chapter 4, the THz emission from nanoparticle arrays is much stronger when the sample is illuminated at oblique incidence. Our experiments show that for all the structures we tested, arrays of nanoparticles and nanoholes and semicontinuous metal films, similar angle dependencies were obtained with little or no signal at normal and grazing incidence and the maximum of the THz intensity at angles of incidence in the range 40° - 60°. A similar angle dependence was also reported for planar gold films [92]. Moreover, our experimental results indicate that the shape of the angle dependence does not depend on the material, silver or gold, and also is not sensitive to sample morphology. The experimental results lead to the conclusion that the observed angle dependence is not related to the microscopic mechanism of the THz generation but rather is due to propagation of the emitted radiation.

In Chapter 5 we discussed the mechanisms of THz generation from plasmonic structures. We showed that two distinct mechanisms might be responsible for THz generation in different intensity regimes, optical rectification on metal surfaces and radiation of the accelerated charges due to the liberation and subsequent acceleration of electrons from the metal by high electric field in proximity to metal surfaces. However, irrespective of the exact mechanism of THz generation, the angular distribution of the THz radiation in the far field can be described in the same approach due to large wavelength of THz radiation.
Namely, we treat the whole THz source as an array of THz dipole emitters. In addition, the observed suppression of the THz signal from plasmonic structures in the far field when the structures are illuminated at normal incidence leads to a conclusion that the dipoles are mainly oriented normal to the surface. This dipole orientation leads to non-effective sum up of contributions from different dipoles in the far field. Thus, if THz generation is measured in the direction of incident pulse propagation, then the measured intensity would be zero, since dipoles emit radiation in the direction perpendicular to their moments. Instead, if the detector is placed in the direction of the highest emission efficiency, perpendicular to the dipole moments, the fields from all the dipoles in far field cancel out due to the absence of retardation between different dipoles. To overcome this problem a special sample design is required. This situation is in many ways analogous to THz generation via the photo-Dember effect, where greater emission of THz radiation for normal incidence excitation can be achieved by applying a strong magnetic field [178], resulting in realignment of the THz dipole moments.

To circumvent the above mentioned problem we fabricated a sample by patterning the semicontinuous silver film. The results obtained from structured sample are compared with those acquired from an analogous unstructured sample. A uniform sample is fabricated by evaporation of 15 nm of silver under vacuum below $10^{-5}$ mbar at a deposition rate of 1 Å/s onto cleaned glass substrates. It was shown previously [104, 105] (see also Chapter 4) that silver films with thicknesses less than 20 nm can generate THz radiation when illuminated with femtosecond laser pulses. The structured sample is fabricated by evaporating 15 nm silver layer through a mask with bars and gaps of equal widths, 300 μm, giving a 1:1 array with period 600 μm.

For THz generation and detection we use 100 fs laser pulses with a central wavelength of 800 nm from an amplified Ti:sapphire laser in a standard THz-TDS setup (see Chapter 2). The focused (1.5 mm) beam has an intensity of order of 10 GW/cm². This pump intensity was used for all the experiments reported in this Chapter. The sampling technique, similar to the one used in the previous Chapters, was used to measure the transient THz field. The recorded time-domain signal is used to retrieve the radiation spectrum by means of a
Selective THz frequency generation from microstructured SMF

Fourier transform. To reduce the absorption of THz radiation by water vapour the setup is placed in closed box filled with dry air.

7.2 Dipole model for THz emission pattern

In this section we provide a simple model which describes the emission pattern of a phase-coupled array of dipoles at an interface. For the sake of simplicity, we consider a linear array of dipole emitters continuously distributed along the line, see Figure 7.1.

![Figure 7.1](image)

Figure 7.1. Schematic representation of the modelled unstructured sample. The incidence and detection angles are designated as $\alpha$ and $\theta$, respectively.

The resulting far-field distribution $E(\theta)$ of an array of dipoles is a product of the radiation pattern (RP) of a single dipole $\Phi(\theta)$ and the directivity factor of the system of emitters $F(\theta)$, which accounts the interference of the radiation from all the emitters, $E(\theta) = \Phi(\theta)F(\theta)$. The second term can be expressed as follows

$$ F(\theta) = \int_{-L/2}^{L/2} A(x) \exp(ikx \sin \theta) dx, \quad (7.1) $$

here $x \sin \theta$ is the difference in the beam paths of the radiation emitted at origin and at coordinate $x$, where $\theta$ is the detection angle; $A(x)$ is the amplitude-phase field distribution along the illumination spot of the size $L$, $k = 2\pi / \lambda_{\text{THz}}$ is the wavenumber of the THz radiation. To simplify the model, we assume a uniform distribution of incident light intensity along the illumination spot. While
the amplitude of the excitation intensity is uniform, its phase \( \phi \) depends linearly on the coordinate, 
\[ \phi(x) = -kx \sin \alpha, \]
where \( \alpha \) is the angle of incidence, as defined in Figure 7.1. Thus \( A(x) \) can be expressed as

\[ A(x) = A_0 \exp(-ikx \sin \alpha), \quad (7.2) \]

where \( A_0 \) is the linear density of the emitted field strength.

![Figure 7.2. Directivity factor as a function of the detection angle \( \theta \) for the angle of incidence \( \alpha = 0 \). The lines correspond to the frequencies 0.33 THz (blue), 0.5 THz (red) and 1 THz (black). The spot size \( L = 1.5 \text{ mm} \).

Using the expression (7.2), the relation (7.1) can be rewritten in the form

\[ F(\theta) = \int_{-L/2}^{L/2} A(x) \exp\left(ikx(\sin \theta - \sin \alpha)\right) dx = A_0 L \frac{\sin \psi}{\psi}, \quad (7.3) \]

where \( \psi(\theta) = \frac{1}{2} k L (\sin \theta - \sin \alpha) \). The function \( \sin \psi / \psi \) reaches its maximal value of 1 at \( \psi = 0 \), i.e. when \( \sin \theta = \sin \alpha \Rightarrow \theta = \alpha \). This means that the directivity factor is maximal in the pass-through detection setup, i.e. when the THz detector is placed on the line of incident excitation beam. Another feature of the pass-through detection setup is the frequency independence of the directivity factor in this configuration. In Figure 7.2 the function (7.3) is plotted for 3 different wavelengths 0.33 THz, 0.5 THz and 1 THz versus the detection angles with the angle of incidence \( \alpha = 0 \). It can be seen from Figure 7.2 that only in pass-through detection setup does the radiation in the far field from all the dipoles comes up in phase. For any other detection configurations the directivity factor is frequency-selective due to interference between the emitters.
Selective THz frequency generation from microstructured SMF

Figure 7.3. Time-domain signals (a) and pulse spectra from semicontinuous silver films measured for two polarizations, p (black) and s (red). S-polarized signal in (a) is scaled by a factor of 30.

The model described above deals only with p-polarized THz radiation, i.e. emitted with the electric field in the plane of incidence. Only for this polarization an excitation phase $\varphi(x)$ depends on the angle of incidence, which leads to a constructive interference in the far field in the pass-through detection setup. For dipoles distributed along the rotation axis in the plane of the sample there is no excitation phase difference and thus the far fields from these dipoles interfere destructively. This corresponds to the case when $\alpha = 0$ in Eq. (7.3), which leads to polarization of THz radiation in plane of incidence (p-polarization) for any incident light polarization states. We found in experiment (Figure 7.3) that THz radiation from silver films is indeed highly polarized in the plane of incidence for any incidence polarization state. The orthogonal s-polarization intensity is about three orders of magnitude weaker.

7.3 Angle dependence of THz generation

Let us now consider the radiation pattern of the Hertzian dipole emitters with the moments oriented perpendicular to the surface. Since the THz electric field is proportional to the second time derivative of the polarization [75], $E \sim \ddot{P} / \ddot{t}^2$, the density of the radiated intensity generated in a small solid angle $d\sigma$ is expressed by the formula

$$d\Phi^2(\theta) \sim N \ddot{d}^2 \sin^2 \theta d\sigma,$$

where $d$ is the dipole moment of the emitter and $N$ is the density of the emitters. The element of the solid angle $\sigma$ can be expressed as $d\sigma = 2\pi \sin \theta d\theta$. Taking into account the last expression, together with the fact
that the collection angles of the parabolic mirrors in the setup are small, the expression (7.4) can be rewritten as,

\[ \Phi^2(\theta) \sim N\tilde{d}^2 \sin^3 \theta. \]  

(7.5)

The product of the density of dipole emitters and the second order time derivative of the dipole moment is proportional to the intensity of THz radiation, which in turn is proportional to the \( n^{th} \) power of the incident intensity \( N\tilde{d}^2 \sim I_{\text{THz}} \sim I_{\text{opt}}^n \) (see section 4.5). Here \( I_{\text{opt}} \) is the intensity of the incident light and \( n \) is the effective order of the process. Since the incident optical intensity on the sample surface is inversely proportional to the spot size, we write

\[ I_{\text{opt}}(\alpha) = I_0 S_0 / S(\alpha) = I_0 S_0 / (S_0 / \cos \alpha) = I_0 \cos \alpha, \]

where \( I_0 \) is an intensity of the incident light in the beam. Combining the last two expressions and assuming pass-through detection setup, i.e. \( \theta = \alpha \), the angle dependence of the RP is then given by

\[ \Phi^2(\alpha) \sim I_0^3 \sin^3 \alpha \cos^n \alpha. \]  

(7.6)

Figure 7.4. (a) The intensity of THz radiation as a function of the angle of incidence for unstructured sample. The dotted line represents a fit with \( n = 3 \), the dashed line corresponds to \( n = 5 \). (b) THz spectra from unstructured semicontinuous silver film in pass-through detection setup for angles of incidence ranging from 5 deg to 40 deg with 5 deg step. Inset: time-domain signal for angle of incidence of 40 deg.

We did not assume any specific THz generation mechanism in the derivation of expression (7.6). Thus, this relation is applicable to both optical rectification on metal surfaces [104] and electron emission [93]. The only assumption was used in our analysis is that the dipoles are oriented normal to the surface. We note, that for samples having in-plane symmetry, the radiation from dipoles with moments oriented along the surface, if they are present, cancels out in the far
Selective THz frequency generation from microstructured SMF field. Therefore, such components of dipole moments could be ignored. This leads to a very little if any THz radiation intensity generated when films are illuminated at normal incidence. At oblique illumination the emission gradually increases with the angle of incidence.

This prediction can be demonstrated experimentally by measuring the angle dependence of THz intensity in pass-through detection setup. The results are shown in Figure 7.4a together with the fit by Eq. (7.6) with two different values of the nonlinearity parameter $n = 3$ and $n = 5$. These numbers represent the range of the effective orders of the process found for THz intensity dependences on incident optical intensities for low energy pulses (see Chapter 4). One can see from Figure 7.4a that there is an optimal angle for THz generation, $\alpha \approx 50 \, \text{deg}$, with low intensities generated at both normal and grazing incidence.

![Figure 7.4a](image)

Figure 7.4a Angle dependence of the THz electric field strength for the range of incidence angles between $-80^\circ$ and $80^\circ$. (b) The time-domain signals, obtained at the angles +60 deg (black) and -55 deg (red).

In the pass-through detection setup, the radiation fields from all the dipoles are in phase, Eq. (7.3), and thus the directivity factor $F(\theta)$ does not depend on the angles $\theta$ and $\alpha$. Since the radiation pattern $\Phi(\theta)$ does not depend on the angle of incidence either, it is expected that the radiation spectra do not depend on $\alpha$. It can be seen from Figure 7.4b that the measured THz radiation spectra are scaled in amplitude as a function of the angle of incidence without any change in their shape.

The scan of the THz signal vs angle of incidence for a range of incident angles from -80 to 80 degrees (Figure 7.5) reveals an inversion of the generated field.
phase without a change in its absolute value of the amplitude. The absence of the strong intensity radiation at normal incidence illumination suggests that the radiation from the dipoles with a moment parallel to the surface is negligible. Indeed, the THz intensity at $\alpha = 0$ is more than 3 orders of magnitude weaker than the maximum intensity at $\alpha = 50$.

### 7.4 Unstructured silver film

Let us now consider the properties of the radiation detected in the direction of $\theta = 90$ degrees for normal incidence excitation. For simplicity we call this detection configuration as *perpendicular detection setup*. The emission efficiency for a single dipole is maximal in this direction. However, in the limit when the excitation spot size $L$ is significantly larger than the THz radiation wavelength, the radiation fields along the sample surface from different dipoles cancel out in the far field due to destructive interference between the dipoles. In Figure 7.6a we present measurements of the THz time-domain signal from unstructured sample obtained in the perpendicular detection setup with the sample being illuminated at normal incidence. The frequency-domain signal is shown in Figure 7.6b. As expected, THz intensity is rather low in this detection configuration. Moreover, the spectrum exhibits a clear oscillatory pattern as a function of frequency. This behaviour occurs due to a finite size of the excitation spot in the sample, and thus the frequencies of the peaks depend on the spot size $L$.

![Figure 7.6](image)

Figure 7.6. (a) Time-domain signal from an unstructured silver film in perpendicular detection. (b) Fourier transform of the time-domain signal shown in (a) (solid line) and theoretical spectrum from a dipole model for unstructured film (dotted line).
Selective THz frequency generation from microstructured SMF

The directivity factor can be obtained from the relation (7.3) using values of $\theta = 90^\circ$ and $\alpha = 0^\circ$, resulting in $\psi = \frac{\sqrt{3}}{2} k L = \pi L / \lambda_{\text{THz}}$. To obtain a theoretical prediction for the emitted spectrum, we multiply the directivity factor by the broad spectrum of a single emitter extracted from the results of THz generation from a semicontinuous silver film (Figure 7.4b). There are clear similarities between the predicted spectrum from this model (dotted line) and the measured data (solid line), see Figure 7.6b. We note a slight disagreement in the spectral positions of peaks and troughs, especially for frequencies above 0.6 THz, which can be expected for such a simple model. Nevertheless, the origin of the features in the spectrum is clear. According to the Eq. (7.3), the radiation pattern is determined by dimensionless parameter $L / \lambda_{\text{THz}}$. For large sizes of the spot or for short wavelengths the effect of destructive interference will be greater than for small spot sizes or long wavelengths. This effect limits the frequency bands of the spectrum. This results in rather weak emission amplitudes and leads to a very noisy experimental spectrum.

### 7.5 Structured silver film

To overcome this limitation, one can engineer the sample to allow radiation of certain wavelengths to interfere constructively in the direction along the sample surface (or, in principle, in any emission direction). This allows us to generate constructive interference of THz radiation in a direction perpendicular to the dipole moment and thus optimize the emission intensity. The simplest way to do this is to remove dipoles which provide an out-of-phase contribution in the far field. This is done by structuring the material in strips, as depicted in Figure 7.7a. For wavelengths equal to the period of the strip array, constructive interference of dipole fields is now possible. It is important to note that this approach works only for a specific wavelengths and frequencies defined by the design of the structure, i.e. the structure acts as a selective frequency generator. To demonstrate this idea we fabricated the structured sample shown in Figure 7.7a and measured the THz radiation in the perpendicular detection setup. The results obtained for this sample are shown in Figure 7.7b and c. We now see a strong emission peak at $\sim 0.5$ THz as expected from the spatial period of the structure.
One can get insight into this behaviour by considering the directivity parameter for the structured sample, describing it as a set of the uniform strips with thickness $b = 300 \, \mu m$ and period $d = 600 \, \mu m$, see Figure 7.7a. Then the directivity factor for the sample can be expressed as a geometric series

$$\sum_{n=1}^{N} F_{sl} e^{i(n-1)\xi} = F_{sl} \frac{e^{i\xi N} - 1}{e^{i\xi} - 1}, \quad (7.7)$$

where $F_{sl} = A_L \sin(\psi)/\psi$ with $\psi = \frac{\kappa}{2} kb (\sin \theta - \sin \alpha)$ is the radiation from a single strip, $\xi = kd (\sin \theta - \sin \alpha)$, and $N$ is the number of the illuminated strips, in our case $N = 3$.

The following transformation can be applied to the expression (7.7):

$$\frac{e^{i\xi N} - 1}{e^{i\xi} - 1} = \frac{e^{i\xi n/2} (e^{i\xi n/2} - e^{-i\xi n/2})}{e^{i\xi/2} (e^{i\xi/2} - e^{-i\xi/2})} = e^{i\xi (N-1)/2} \frac{\sin(\xi N/2)}{\sin(\xi/2)}. \quad (7.8)$$

Figure 7.7. a) The sketch of the structured silver film. (b) The time-domain signal from the structured silver film in perpendicular detection setup. (b) Fourier transform of the time-domain signal (solid line) shown in (b) and the theoretical spectrum from a dipole model for structured film (dotted line).
Finally, combining the results from expressions (7.7) and (7.8) for the amplitude of the directivity factor, the following expression is obtained

\[ F(\theta) \sim \left| \frac{\sin(\psi) \sin(N_\xi/2)}{\psi \sin(\xi/2)} \right| \]  

(7.9)

The theoretical results from the expression (7.9) for normal incidence illumination \((\alpha = 0^\circ)\) and perpendicular detection setup \((\theta = 90^\circ)\) are compared with the experimental results in Figure 7.7c. Experiment and theory agree well, particularly for the dominant emission peak at \(\sim 0.5\) THz. At this frequency, for the same excitation fluence, the radiation intensity emitted by the microstructured sample is 25 times greater than from the unstructured film, despite the two-fold decrease in active surface area.

### 7.6 Summary and conclusions

In this section we reported on our investigations of microstructured semicontinuous silver films designed to generate resonant THz frequencies under femtosecond laser pulse illumination with resonant frequencies defined by the sample geometry. By patterning the film into an array of microstrips, we showed that one can achieve constructive interference of THz emission in a direction perpendicular to the emission dipole. This results in the microstructured film emitting a significantly greater spectral density of the THz radiation intensity when compared to an unstructured film. To understand our results we developed a simple analytical model based on the field distribution for an array of THz dipole emitters. The model describes some of the main features of the generated THz radiation, including the angle dependences of the emitted radiation patterns and the resonant features of the emission spectrum.
Conclusions and outlook

Summary and conclusions

This thesis is focused on the interaction of ultrashort laser pulses with metal nanostructures. Particularly, the effects of coherent acoustic oscillations in nanoparticles and the generation of THz pulses on metal surfaces after femtosecond laser pulse excitation were examined.

The results of the investigations of the coherent acoustic vibrations in the arrays of nanoparticles are reported in Chapter 3. We investigated how the fundamental breathing mode frequency alters with the particle height. The weak dependence of the period of oscillation on the particle thickness confirms the lateral character of the particle deformations. We also measured the vibrational particle response due to particle deformation, both symmetrical and asymmetrical. It was found that even a minor asymmetry in the particle shape significantly reduces the quality of its oscillation. In addition, we showed a high sensitivity of the particle response to the surrounding media, and in particular to thin metal overlayers.

The Chapters 4 – 7 deal with the generation of THz radiation upon femtosecond laser pulse illumination from different structures: arrays of nanoparticles and nanoholes, and semicontinuous metal films. Two materials were mainly used, silver and gold. After a first observation of THz generation in 2004, several reports were published investigating the effect. To explain the phenomena two different mechanisms were proposed, optical rectification on metal surfaces and electron emission with subsequent electron acceleration by ponderomotive forces. However, neither was able to explain all the observed features. In our investigations we tried to clarify which mechanisms are involved and what conditions control THz generation from plasmonic structures. The results are summarized below.

In Chapter 4 the generation of THz radiation from semicontinuous metal films and ordered arrays of nanoparticles were investigated. By varying the thickness of SMF we found that the strongest THz field is generated around the percolation threshold, at metal concentrations where the highest average near field enhancement is achieved. These results correlate well with the SERS
measurements carried out on such films. The ordered arrays of nanoparticles were used to further clarify the link between the THz generation efficiency and the near field strength. By varying the nanoparticle height we were able to controllably shift the plasmon resonance wavelength. The THz measurements were accompanied with computer modelling of the near field distribution around the particles. The results clearly show that the highest THz field is generated by structures with the strongest field enhancement.

We also explored the dependence of the THz fluence on the pump power. The results show a high-order dependence at low range of incident intensities, which rules out optical rectification as a mechanism for THz generation in this regime. The order of the process and the similarity between the dependences of the THz fluence and the electron emission current on incident intensity suggest the accelerated motion of the emitted electrons, as has recently been proposed, as a mechanism for THz generation in the range of pulse energies used in the experiments. In addition, a simple model based on the electron emission allowed us to explain the main features of the observed intensity dependence.

To investigate the phenomenon of THz generation from plasmonic structures further, and to find evidence of another proposed mechanism, optical rectification on metal surfaces, we performed comparison measurements on two types of plasmonic structures, arrays of nanoparticles and nanoholes. These results are reported in the Chapter 5. In addition to the bimodal dependence observed from nanoparticles, the nanoholes show an extra regime with a low-order dependence at incident intensities below 5 GW/cm², in the region where the high-order dependence is expected based on the electron emission mechanism of THz generation. The low-order dependence reveals a generation mechanism which is assumed to be the optical rectification mechanism reported in some THz generation experiments on metal films. We corroborate these results with the electron emission data, which suggest that THz generation in this region of incidence intensities cannot rely on electron emission. We support our findings with computer modelling which is used to explain some peculiarities in the observed order dependences. Our results add weight to the recent suggestion that both proposed mechanisms can be responsible for THz generation from plasmonic structures, each of the mechanisms may be dominant in its own range of incident intensity. Thus, at
low pump energies in the region where the electron emission current is weak, the THz generation occurs mainly through optical rectification. At higher energies the THz generation through electron emission becomes the main contributing mechanism.

The high-order dependence of the THz fluence on incident intensity makes the effect of THz generation very sensitive to changes in the near-field strength. In our measurements of the THz generation efficiency at low temperatures reported in Chapter 6, we found a very strong dependence of the THz intensity on the temperature in some samples. We explain this effect through a reduction of the plasmon resonance damping, especially the suppression of the electron-phonon scattering at low temperatures. The high sensitivity of the THz generation to changes in the imaginary part of the metal dielectric function makes the effect suitable for the investigation of SPP damping mechanisms as well as the interaction of plasmonic structures with gain media.

The angular distribution and polarization properties of the THz radiation in the far field were studied in Chapter 7. The simple model based on the field distribution for an array of THz dipole emitters is used to explain the main features of the THz fluence dependence on the illumination angle. We also showed that the destructive interference of the radiation generated from different parts of the sample reduces the efficiency of the generation process. To overcome this problem we fabricated a microstructured semicontinuous silver film, producing higher THz intensity at the resonant frequencies defined by the sample geometry as compared to unstructured sample. The developed dipole-array model is successfully applied to explain the spectral features of the emission spectrum.

**Further work**

The research presented in this thesis leaves a number of open questions which require further investigation.

In experiments on THz generation from plasmonic structures we observed a high-order dependence of the THz fluence on incident intensity, an effect that is still not properly explained, in particular the deviation of the predicted order dependence from that obtained in the experiment. To explain this feature and to better understand the main properties of the THz generation process, computer
modelling of the phenomena is required to calculate the near-field distribution in the vicinity of the metal surfaces and the dynamics of the emitted electrons. Knowing the electron dynamics allows for an evaluation of the characteristics of THz radiation due to the accelerated movement of electrons. This can specify the intensity range in which the THz generation can be based on electron emission.

The pressure and temperature effects in THz generation also need further investigation. The following two sets of experiments may shed light onto the mechanism of the THz intensity temperature dependence. In the first set of experiments two types of measurement have to be produced on the ordered arrays of nanoparticles with controllably varying plasmon resonance, the measurements of the THz intensity temperature dependence and the transmission spectra from these particle arrays at different temperatures. In the second set of experiments the THz intensity and electron emission current have to be measured as a function of temperature from the same plasmonic structures. If similar dependences are obtained for both effects, it would provide further evidence of the electron emission mechanism of THz generation. In addition, the temperature reduction may enhance many other effects relying on the near field enhancement, such as SERS, SHG, THG, metal-enhanced fluorescence and others.

To understand the phenomenon of THz generation from plasmonic structures better, more efforts are required. This could also improve the THz generation efficiency. There are two main approaches that can be used to achieve this. The first approach concerns the design of the structures with higher field enhancement, since the THz generation is extremely sensitive to the strength of the near fields. It is even plausible that after some optimisation one could use a single metallic nanoparticle as a local THz emitter. In the second approach the efforts should be applied to design 2D and even 3D arrays giving optimal THz emission. Thus, suppressing the effects of destructive interference from different THz sources at normal incidence should significantly increase the THz generation efficiency.
Publications and presentations

Publications


Conference papers


Other conference contributions


References


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