Tailoring grating strip widths for optimizing infrared absorption signals of an adsorbed molecular monolayer

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Abstract: Metal structures with resonances in the mid-infrared spectral range enable an increased sensitivity for detecting molecular vibrational signals. 1D gold strip gratings have already proven potential in surface-enhanced infrared absorption (SEIRA) experiments, as grating resonances and local electric field enhancement can be spectrally tuned by changing the grating period. Here, we identify the grating strip width as another important design parameter, which is investigated for further optimization of molecular absorption signal enhancement in SEIRA experiments. Previous literature used gratings to increase light absorption in relatively thick polymer layers. Here, we demonstrate the capability of gold strip gratings fabricated on a CaF₂ substrate to enhance the CH₂ vibrational modes of a thiol-based monolayer of MHDA. An optimal choice of the strip width \( w = 1.33 \mu m \) enables a maximum vibrational signal enhancement factor of around 84, when normalized to microscopic GIR measurements of an MHDA monolayer on an extended gold surface. Numerical simulations demonstrate the broadband local field enhancement of gold strip gratings, which are suitable for enhancing multiple vibrational modes in a large hot-spot volume.

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1. Introduction

Infrared spectroscopy enables a non-destructive and label-free characterization of matter [1]. In surface enhanced infrared absorption (SEIRA) spectroscopy, spectral signatures of molecular vibrations can be detected beyond monolayer sensitivity by using tailored metallic structures, which couple free space radiation into regions of sub-wavelength size [2]. Local electric field enhancements occur and enable an increased absorption by molecules which are placed in these so called "hot spots" [3]. Surface lattice resonances and near-field coupling can be exploited to significantly increase the SEIRA signals by using periodic arrangements of antennas and small gaps between antenna tips [4–7]. Usually, antenna (array) resonances are tailored by changing the antenna lengths to spectrally match the maximum local field enhancement with the vibrational modes of interest [8]. Besides the prominent rod antennas, several other antenna structures are proposed as SEIRA substrate, such as e.g. cross structures [9], split ring resonators [10], triangles [11, 12], fan-shaped antennas [13] and vertical antennas [14, 15]. A comprehensive overview on antenna structures for SEIRA can be found in recently published review papers [2, 7]. Each antenna structure can have individual advantages and disadvantages in different SEIRA experiments. For example, fan-shaped antennas in a metal-insulator-metal geometry or vertical antennas with sharp tips can provide exceptionally high local field enhancements in tiny hot spots. For low concentrations of analyte molecules and their successful delivery to the hot spot volume, these structures are a good choice for SEIRA experiments. Yet, such structures may be inappropriate for a combination with in-situ SEIRA measurements in a microfluidic setup. For SEIRA measurements in microfluidic environment, typically, infrared transparent windows
are used for reflectance measurements through the loss-less dielectric substrate [16, 17]. A comparably low but spatially extended and uniform field enhancement is achieved by grazing incidence reflectance (GIR) or thin film based substrates and can be exploited efficiently to enhance light absorption of likewise extended analyte films or layers [18, 19]. An amount of analyte less than a dense monolayer but more than a sparse amount of molecules may favour a hot spot volume and local field enhancement such as provided by discs or 1D gratings [17, 20, 21]. Gold strip gratings provide a broadband local field enhancement and a large hot spot volume. The broadband field enhancement is suited to enhance absorption of spectrally distributed vibrational bands (cf. Fig. 3(b) in [20]). The large hot spot volume allows adsorption of many molecules, which can compensate for the lower peak field enhancement. Gold strip gratings can be fabricated by standard UV lithography and their compatibility with electrochemical impedance spectroscopy (EIS) and surface plasmon resonance (SPR) sensors can combine quantitative information regarding mass adsorption with the specific information obtained by SEIRA [20, 22–24].

In this work, we investigate and improve the design of 1D gold strip gratings for SEIRA. Similar to antenna arrays, gold strip gratings can be tuned by changing the periodicity or the illumination direction [4, 21, 25, 26]. In analogy to the antenna length, the local field enhancement of a gold strip can be tuned by changing the gold strip width. The gold strip width is varied in SEIRA experiments targeting the symmetric and asymmetric stretch vibrations of CH$_2$ groups in a self assembled monolayer (SAM) of thiol-based molecules. Having studied the influence of periodicity on the SEIRA performance of gold strip gratings in our previous publication [20], here, we demonstrate a peak of the SEIRA signal when optimizing the strip width for a given periodicity. Thus, the strip width is identified to be an important design parameter for sensing experiments with gold strip gratings.

2. Working principle of resonant strip gratings

Gold strip gratings are simple 1D metallic surface lattices as sketched in Figs. 1(a) and (b). Focussed ion beam (FIB) milling using a FEI Helios NanoLab DualBeam system is applied to prototype different gold strip gratings by cutting the gaps $g$ in a thermally evaporated gold film. The grating structures have a lateral size of about 50 $\mu$m $\times$ 70 $\mu$m and thus always contain several tens of gold stripes. The grating has a periodicity $p$ and the stripes have a height $h = 35$ nm and a certain width $w$. CaF$_2$ is used as dielectric substrate material with a refractive index $n$ around 1.4 in the mid-IR spectral range [11]. Generally, such periodic structures give rise to diffraction orders resulting from constructive interference of light scattered by the individual elements of the surface lattice into certain solid angles. The interplay between momentum components of the incident light and the light scattered into diffraction orders as well as the momentum offered by the surface lattice must obey the general law of momentum conservation, as described by the Laue-condition [27, 28]:

$$\vec{k}_{\text{scat}} || = \vec{k}_{\text{inc}} || + \vec{G},$$

(1)

where $\vec{G}$ is a reciprocal lattice vector, $\vec{k}_{\text{scat}} ||$ and $\vec{k}_{\text{inc}} ||$ are the projections of the wavevectors of the incident and the scattered light on the surface lattice plane. This equation states, that the momentum of the incident light projected to the surface lattice plane can be reduced or increased by multiples of a reciprocal lattice vector. By solving the Laue-condition, the grating resonance wavelengths of a 1D grating can be calculated by

$$\lambda_{(j \ 0)} = p \frac{n_{\text{scat}}}{|j|} \frac{n_{\text{inc}} sin (\theta_{\text{inc}})}{j},$$

(2)

where $p = p_x$ is the grating period, $\theta_{\text{inc}}$ is the angle of incidence and $j$ is an integer defining the grating order [25]. The refractive indices $n_{\text{scat}}$ and $n_{\text{inc}}$ correspond to the refractive index of the upper or lower half-space, depending on the illumination and scattering direction. In Fig.
Fig. 1. (a) Cross-sectional view (x-z-plane) of a gold strip grating on a CaF$_2$ substrate with indicated parameters: grating period $p$, gap $g$, strip width $w$ and strip height $h$. An oblique incidence is indicated by the polar angle $\theta$. The electric field vector is in the plane of incidence. (b) Illustration of the fundamental charge carrier oscillation in the grating stripes with indicated coordinate system. (c) Grating analysis (top panel) of gold strip grating reflectance measurement (bottom panel). The calculated spectral positions of the grating resonances at the average polar angle of incidence ($\theta = 17^\circ$) are related to measured reflectance peaks.

In (a), the x-component of the wavevector of the incident light along the lattice direction ($k_x$) is indicated together with the projected wavevector ($\mathbf{k}$), which can have a tilt $\theta$ from the surface lattice normal. The incident light must be polarized in x-direction to excite the fundamental charge carrier oscillation in the gold stripes as sketched in the 3D representation in Fig. 1(b). FT-IR reflectance measurements are performed with a Bruker Vertex 70 spectrometer and a Hyperion 2000 microscope using 15× ($NA = 0.4$) Schwarzschild objectives, a liquid nitrogen cooled MCT detector and a wire grid polarizer to ensure a high amount of polarization in x-direction. The spectra are recorded with at least 256 scans and a resolution of 2 cm$^{-1}$ and are normalized with respect to the reflectance of the surrounding gold film. Fig. 1(c) analyses the normalized FT-IR reflectance spectrum of a gold strip grating having a period $p = 1.95$ μm and a strip width $w = 1.33$ μm. The spectral positions of grating resonances according to Eq. (2) can be related to the measured peaks in the reflectance spectrum by assuming an average angle of incidence $\theta = 17^\circ$. The reflectance peak width is mainly influenced by the angular dispersion of grating resonances in combination with the angular range of the microscope objective, which hinders a direct conclusion on the local field enhancement from far-field reflectance measurements. Besides e.g. scanning near-field optical microscopy (SNOM), which can directly access the near-fields of metal structures [29], SEIRA can be used as a method for probing the local field enhancement of metallic structures [30].
3. Optimization of the grating strip width for SEIRA

3.1. Numerical simulations of a single strip

In order to quantify the local field enhancement of single gold strips, we compare the gold strip with a single gold rod antenna and investigate the dependence of the local field enhancement on the strip width \( w \). We perform simulations using CST Microwave Studio, a commercial software with a finite integration technique (FIT) solver which numerically solves Maxwell’s equations with respect to the given boundary conditions. Local field enhancement in the vicinity of metal structure is expected at those sidewalls, where charge carriers accumulate. In Fig. 2(a), local near-field enhancement spectra are simulated at 1 nm distance from single gold structures located on a lossless CaF\(_2\) substrate. The gold structures are chosen to have a fixed width \( w = 1 \) µm, a fixed height \( h = 35 \) nm but a varying extension \( L \) in y-direction. From small to larger values of \( L \), the structure evolves from a rod antenna to a gold patch, as shown by inset sketches. Additionally to the structure geometry, also the charge carrier distribution of the excited fundamental resonance is sketched. The sharpest resonance lineshape is simulated for the rod antenna structure having a width of \( w = 0.2 \) µm and a maximum local near-field enhancement factor close to 40. With increasing \( L \), the local field enhancement resonance broadens, shifts to higher wavelength and the maximum local field enhancement drops below 15. In Fig. 2(b), local near-field enhancement spectra are simulated at 1 nm distance from single gold stripes \((L \to \infty)\) with varying width \( w \), also located on a CaF\(_2\) substrate. The simulated single gold strip resonances shift to lower wavenumbers and the peak local field enhancement slightly increases with increasing strip width \( w \). Increasing \( w \) from 0.45 µm to 1.8 µm, having a grating period of 1.95 µm, shifts the single strip resonance wavenumber from 5000 cm\(^{-1}\) to about 1300 cm\(^{-1}\). Although the resonances are broad and the peak local field enhancement is lower compared to a rod antenna, the numerical simulations suggest the need of tailoring of the strip width \( w \) in combination with the period \( p \).

3.2. Strip-width variation in gold strip gratings

For an experimental investigation, gold strip gratings with different strip widths \( w \) are fabricated. Example scanning electron microscopy (SEM) images of the structures are shown in Fig. 3(a). The gratings are designed to have a period \( p = 1.95 \) µm in order to tune the field enhancement...
Fig. 3. Strip width \( w \) variation of gold strip gratings having a fixed period \( p = 1.95 \) µm. (a) SEM images of gold strip gratings on a CaF\(_2\) substrate. (b) Measured reflectance spectra. The green shaded bar marks the spectral region of CH\(_2\) vibrational modes. (c) Comparison of simulated local field enhancement spectra at 1 nm distance from the stripes for a single stripe (dashed curves) and a grating (solid curves) for two different strip widths. (d) Simulated reflectance spectra with the geometries deduced from the experimental structures presented in (a). The dashed vertical lines mark spectral positions of the grating resonances corresponding to the air and CaF\(_2\) half-spaces.

provided by the \((-1 0)\) CaF\(_2\) grating resonance to the spectral position of CH\(_2\) absorption bands [20]. While the period remains constant, the strip widths \( w \) range from 0.25 µm to 1.69 µm. Thus, the smallest gap is larger than 250 nm and near-field coupling can be neglected. Exemplary reflectance spectra are presented in Fig. 3(b). The overall reflectance increases with increasing strip width \( w \), which is in agreement with the simulated reflectance spectra in Fig. 3(d). The sharp peaks and features in the simulations compared to the broad peaks and features in the experiments can be explained by the grating resonance angular dispersion. The simulations use a single polar angle \( \theta = 17^\circ \) in contrast to a large set of angles present in the microscopic measurements. The measured \((-1 0)\) CaF\(_2\) reflectance peak of the \( w = 1.69 \) µm grating is shifted to lower wavenumbers compared to the analytically calculated spectral position of the first grating resonance, while the corresponding reflectance peak of the \( w = 1.0 \) µm grating is shifted to higher wavenumbers compared to the analytic calculation. Thus, the exact spectral position of the reflectance peaks in the experiments is influenced by the spectral position of the single strip resonance, which is spectrally shifted for different gold strip width \( w \). The simulated local field enhancement presented in Fig. 3(c) compares two different strip widths as well as the single strip and the grating case. The simulated local field enhancement of single gold strips, as presented with dashed curves in Fig. 3(c), is lower than the grating case in the whole examined spectral...
range. Peaks in the local field enhancement occur in spectral vicinity of the grating resonances, as demonstrated by vertical dashed lines calculated from Eq. (2). The charge carrier oscillation in the stripes as sketched in Fig. 1(b) causes the stripes to radiate mainly perpendicular to the surface lattice. This supports far-field interference effects but unfortunately prohibits an efficient radiative coupling between the grating strips. While radiative coupling can increase the local field enhancement factor by an order of magnitude for rod antenna arrays compared to single rods [4], it is a factor of around 1.5 for the $w = 1.0 \mu m$ grating compared to the corresponding single strip at the (-1 0) grating resonance. The local field enhancement of the $w = 1.0 \mu m$ grating exceeds the local field enhancement of the $w = 0.64 \mu m$ grating at the spectral position of the (-1 0) grating resonance, while it is the other way around at the spectral position of the (1 0) grating resonance wavelength. This can be explained by the shift of the single strip resonance. The larger strip width of $w = 1.0 \mu m$ offers higher local field enhancement for the grating at lower wavenumbers while the smaller strip width of $w = 0.64 \mu m$ enhances local fields more efficiently at higher wavenumbers.

### 3.3. Strip-width dependent SEIRA experiments

In order to experimentally probe the strip width dependent local field enhancement of gold gratings, we couple charge carrier oscillations with molecular vibrations. In such SEIRA experiments, we do not only probe the local field enhancement but simultaneously we can quantify and improve the sensing capability of gold strip gratings. Thiols can form a well ordered, self assembled monolayer (SAM) on gold as sketched in Fig. 4(a) for mercaptohexadecanoic acid (MHDA). Besides the sulfur atom that establishes a covalent bond to the gold, the molecule consists of fifteen CH$_2$ groups and a carboxylic end-group. Due to the specific binding to gold, there are no molecules attached to the CaF$_2$ substrate between the gold stripes as sketched in Fig. 4(b). For SAM preparation, the same analyte and procedures are applied as in our previous work [25]. The CH$_2$ groups have a symmetric and an asymmetric vibrational mode at $\tilde{\nu}_{\text{sym}} = 2850 \text{ cm}^{-1}$ and $\tilde{\nu}_{\text{asym}} = 2918 \text{ cm}^{-1}$, respectively. An exemplary reflectance spectrum of an MHDA covered gold strip grating is presented in Fig. 4(c). A cubic spline interpolation is used in order to extract the vibrational signals, whose spectral positions are marked with vertical dashed lines.
Fig. 5. (a) Measured reflectance difference spectra for MHDA covered gold strip gratings having different strip widths \( w \) and a constant period \( p = 1.95 \mu m \). (b) Simulated local field enhancement at 1 nm distance from strips (see red arrow) with different widths \( w \) at \( \tilde{\nu} = 2918 \text{ cm}^{-1} \). (c) Vibrational signals of the symmetric (blue) and asymmetric (red) \( \text{CH}_2 \) stretch vibrations extracted from the reflectance difference spectra of gratings with different strip widths \( w \).

The subtraction of the red-coloured spline interpolation from the original black-coloured reflectance spectrum leads to a reflectance difference spectrum, which reveals the SEIRA signal. Reflectance difference spectra for all the MHDA covered strip gratings with a constant period \( p = 1.95 \mu m \) and varying strip widths \( w \) are presented in Fig. 5(a). Generally, the vibrational signal of the symmetric and asymmetric stretching modes of \( \text{CH}_2 \) can be observed. An additional dip, located at slightly larger wavenumbers than the asymmetric stretch vibration resonance at 2918 cm\(^{-1} \), probably belongs to a vibrational mode of \( \text{CH}_3 \). MHDA does not have a \( \text{CH}_3 \) group, which is why the presence of a \( \text{CH}_3 \) vibrational signature is a hint to contaminants, maybe because the used MHDA powder only has a 90% purity [25]. In case these contaminants prohibit a dense SAM formation or do have additional \( \text{CH}_2 \) bonds, an enhancement factor could be underestimated, respectively. Yet, a change of the vibrational signal strength upon varying the strip width is still reliable indication, as the average number of \( \text{CH}_2 \) bonds at different sidewalls or at different gratings is highly likely to be equal. With the help of the \( L = 1.33 \mu m \) grating spectrum, the further evaluation of the symmetric and asymmetric \( \text{CH}_2 \) vibrational signal is depicted in Fig. 5(a). The vibrational signal is measured from the local maximum to a local minimum of the reflectance difference in the spectral vicinity of the vibrational mode. As a sidenote, the
spectrum for $L = 0.8 \, \mu m$ is grey shaded, because it seemed that a solvent droplet accidentally dried on this grating after MHDA SAM preparation. Much more molecules are deposited at this specific grating compared to the single monolayers of the other gratings. The dependence of the symmetric and asymmetric CH$_2$ vibrational signal on the strip width of the grating is presented in Fig. 5(c). The lines are guides to the eye and the contaminated grating data is shown but not included in the analysis. Thus, maximum vibrational signals of 0.6 % and 1 % are obtained at a strip width of $w = 1.33 \, \mu m$ for the symmetric and asymmetric mode, respectively. The SEIRA signals can be referenced to vibrational signals obtained by a GIR measurement of an MHDA monolayer on an extended gold surface. The vibrational signals obtained in GIR measurements yield 0.2 % and 0.3 % for the symmetric and asymmetric vibrational modes, respectively. Thus, the maximum SEIRA signal enhancement is roughly a factor of 3 for both modes. Considering the different amounts of molecules on an extended gold surface compared to the molecules at a gold strip’s sidewalls, an additional enhancement factor of 28 can be taken into account. In total, the maximum vibrational signal enhancement factor for the CH$_2$ vibrations of MHDA on gold strip gratings in comparison with microscopic GIR measurements of MHDA on a flat gold surface is around $84 = 3 \cdot 28$. Care must be taken when comparing this apparently low value with literature data. Often, in favour of higher numbers, other reference measurements are used to push the numbers, because GIR measurements already provide a vibrational signal enhancement in the order of 16 [7,31,32]. In Fig. 5(b) the local field enhancement is calculated for different strip widths at a wavenumber of 2918 cm$^{-1}$. The peak local field enhancement is simulated at a strip width of $L = 1 \, \mu m$, which is slightly shifted compared to the peak vibrational signals obtained in the experiments. This deviation between simulation and experiment can have several reasons such as the influence of focussing optics in the experiment and differences in the experimental and simulated geometry. An important difference according the geometry could be an undercutting of the gold strips during FIB milling [25]. In case a single strip is on a pedestal, its resonance is expected to be shifted to smaller wavelengths compared to a single strip located on a flat sample surface [33]. Such a blueshift would coincide with a larger strip width $w$ for maximum vibrational signal enhancement at the same frequency.

4. Conclusion

We performed numerical simulations to predict the single gold strip resonance shift upon changing strip width. Although the field enhancement is found to be considerably lower and broadened compared to a single rod antenna, the single strip exhibits a peak local field enhancement which shifts to higher wavelength upon increasing the width. Measured and simulated reflectance spectra of gold strip gratings show a good agreement and the local field enhancement of gold strip gratings is shown to exceed the single strip case in a broad spectral range. The benefits of tailoring the single strip width in gold strip gratings is proven by experimental SEIRA experiments. An optimal choice of the strip width $w = 1.33 \, \mu m$ enables a maximum vibrational signal enhancement factor of around 84 for the CH$_2$ vibrations of MHDA on gold strip gratings in comparison with microscopic GIR measurements of MHDA on a flat gold surface. Principally, gold strip gratings provide a broadband local field enhancement, suitable for enhancing multiple vibrational modes.

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