Theoretical analysis of plasmonic black gold:
periodic arrays of ultra-sharp grooves

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Abstract. Periodic arrays of tapered grooves in gold surfaces are theoretically considered for turning high-reflectivity (shiny) gold surfaces into broadband low-reflectivity (black) surfaces, when illuminated by light polarized perpendicular to the groove direction, by making use of nanofocusing and subsequent absorption of gap-plasmon modes excited in the tapered grooves. The importance of realization of the adiabatic regime of nanofocusing, i.e. without reflection of plasmonic modes by tapered walls, is emphasized, and the taper angle that can be used for a given groove width without causing significant reflection is quantified.

It is shown that nearly parallel groove walls at the groove bottom, i.e. ultra-sharp grooves, are required in order to sufficiently suppress the light reflection. Periodic arrays of V-grooves, and grooves with profiles described by a power-formula, are demonstrated to have much higher reflectivity levels than ultra-sharp groove arrays. Reflectivity spectra of ultra-sharp groove arrays are presented for a wide range of parameters, including the groove depth, bottom groove width, period, width of a flat plateau, and the angle of light incidence. Similar surface geometries in other metals are shown to have higher or smaller reflectivity levels depending on whether the metals are more or less absorptive than gold.
1. Introduction

Surfaces with selective absorptivity and thus emissivity profiles are interesting for solar energy harvesting or for thermophotovoltaics applications. It has been demonstrated recently with surfaces covered with well-defined arrays of a mixture of resonant plasmonic resonators that there is a wide possibility for designing the thermal absorptivity and emissivity profile [1–6]. There has also been focus on another non-resonant type of well-defined geometry for broadband absorption of light using a concept that is referred to as optical black holes. The idea is that, in a geometry where the refractive index increases sufficiently fast towards a centre, light rays passing by will change direction and spiral in towards the centre according to Snell’s law of refraction [7, 8]. This concept has been realized experimentally with a complex meta-material geometry for microwave frequencies [9], and more recently it has been proposed that the same effect could be obtained for gap-surface-plasmon-polariton (gap-SPP) waves with a very simple structure consisting of two touching metal spheres [10], in which case the gap-SPP waves propagating in the gap between metal surfaces will spiral towards the touching point due to a gap-SPP mode effective index that increases rapidly towards the touching point. Two touching cylinders, or a cylindrical void placed inside a metal cylinder and being displaced from the centre, have also been suggested as broad-band light-harvesting devices [11].

Apart from these new approaches to making black materials there is also the more traditional approaches using geometries created by distillation of metals at high pressures [12], the more recent blackening of metals by laser ablation [13, 14], sputtered metal-dielectric compounds [15], and silver particles randomly distributed in a dielectric material [16]. The random nature of such materials makes a precise quantitative theoretical analysis very difficult.

In a recent paper the authors introduced the idea of turning shiny gold surfaces into black surfaces by structuring the surface with a periodic array of ultra-sharp convex grooves [17]. The main explanation for obtaining a very low reflectivity is that light incident on the surface is coupled into gap-SPP waves propagating inside the grooves towards the groove bottom, and with an appropriate choice of groove tapering the gap-SPP waves will not be reflected much but will instead be absorbed in the metal. Because the absorption does not rely on a resonant phenomenon it is possible to achieve broadband absorption. In this paper we will theoretically analyse this type of ultra-sharp geometry and give a quantitative description of how the grooves should be tapered in order to reduce the reflectivity and make the most out of a finite available groove depth. For comparison we will also provide examples for other arrays of sharp grooves,
Figure 1. (a) Black gold geometry that can be made ultra sharp at the bottom by letting the angle $\alpha$ and the bottom groove width $\delta$ approach zero. Except for the flat top region of width $a$ the groove array consists of parts of circles put together such that there are no sharp edges. (b) Periodic array of grooves with the surface of one period described by the power formula $z = H'(1 - [2|y|/\Lambda]^N)$ except that the bottom of grooves is rounded off with part of a circle when the groove width becomes equal to $\delta$.

namely the case of V-grooves, and convex grooves described by a power-formula, that are not sufficiently sharp near the groove bottom to obtain very small reflectivity levels. We will also present some examples of using other metals, namely silver, chromium, platinum, nickel and palladium, being either less absorptive or more absorptive than gold.

The surfaces considered in this paper have the property that they are efficient absorbers for certain short wavelengths while they are efficient reflectors for long wavelengths. Except that the transition wavelength between regimes with efficient absorption or reflection should be shifted to longer wavelengths, which to some extent is achieved in this paper when making metal surfaces more black, the resulting surface reflectivity profile has properties that are similar to the desired reflectivity profile of surfaces used for solar power concentrator applications [18–20].

The paper is organized in the following way. In section 2 we present qualitative and quantitative considerations regarding how to taper grooves in order to obtain a small reflectivity. In section 3 we study the reflectivity from periodic arrays of V-grooves and grooves described by a power-formula. In section 4 the reflectivity from periodic arrays of ultra-sharp grooves in a gold surface is studied considering a wide range of design parameters. In section 5 we consider reflectivity spectra for groove arrays in other metals being either more or less absorptive than gold. We offer our conclusions in section 6.

2. Adiabatic groove tapering method

Two types of periodic arrays of grooves in a metal surface being considered in this paper are presented in figure 1 along with different design parameters allowing control of the groove
design. In the case of figure 1(a) the groove array is characterized by a flat top section of width \( a \) joined with part of a circle of radius \( r \), which is again joined with another part of a circle (of a much larger radius) with curvature determined according to the choice of \( a \), \( r \), period \( \Lambda \), height \( H \), bottom groove width \( \delta \) and bottom groove angle \( \alpha \). For this geometry ultra-sharp grooves can be obtained by letting both \( \delta \) and \( \alpha \) approach zero. Another approach for the design of sharp groove surfaces that we will consider is shown in figure 1(b). In this case one period of the groove geometry is described by the power formula \( z = H'(1 - |2y|/\Lambda)^N \) except for a rounding of the groove bottom with part of a circle at the point where the groove width equals \( \delta \). Note that due to this rounding the actual groove depth \( H \) will be smaller than \( H' \). For this geometry the grooves can be made sharper by increasing \( N \) but it will never be possible to have parallel groove walls at the groove bottom as in the design in figure 1(a) with \( \alpha = 0 \).

The surface geometries and electromagnetic fields are treated as invariant along the \( x \)-axis in the theoretical calculations presented in this paper. All numerical calculations presented in the following sections were made with the periodic Green’s function surface integral equation method [21]. In the numerical modelling we use the dielectric constant of gold from [22]. This means that we use a local-response model for the dielectric constant of gold even though some dimensions, especially near the bottom of the groove, are in the sub-nanometre range. We do expect, however, that if one finds a way to carry out a calculation for the same geometry using a non-local response theory [23–25] that the absorption losses arrived at will be even higher than those calculated here.

The idea behind the black surfaces studied in this paper is that gap-SPP waves are excited near the groove top, and that they are subsequently absorbed during propagation towards the groove bottom as a consequence of propagation losses. This also requires that reflection of the gap-SPP waves can be largely avoided. It is well-known that a thin dielectric slab (or an air-gap) covered with metal on each side supports gap-SPP waves that experience no cut-off with respect to the slab thickness and will exist even in the limit of extremely thin dielectric slab thicknesses approaching zero [26]. As p-polarized light is incident on grooves such as those in figure 1 we expect that a gap-SPP wave is excited near the top of the grooves, and that the gap-SPP will propagate down towards the bottom of the groove along the negative \( z \)-axis adapting gradually to the changing width of the groove towards the groove bottom. During the propagation the gap-SPP will experience a propagation loss due to Ohmic losses in the metal and a reflection that will depend on how fast the groove width decreases along the direction of propagation. Because of the gradually decreasing groove width the power in the gap-SPP wave will be strongly focused or confined in a small region near the groove bottom. Naturally, any tapering strategy where the width of the grooves changes extremely slowly implying also extremely deep grooves can result in excellent absorption of light and practically no reflection. Here, however, we wish to obtain a low reflectivity without having grooves that are deeper than 500–1000 nm. Thus, we need to make the best of the available groove depth.

Reflection of the gap-SPP wave can be avoided by tapering the grooves sufficiently slowly such that the gap-SPP mode index does not change much over the distance of a gap-SPP wavelength. For large air-gap widths of e.g. a half free-space wavelength the gap width can be reduced even by a factor of two without changing the gap-SPP mode effective index by more than a few per cent. In the other end where the gap is extremely small the mode effective index on the other hand will be inversely proportional with the gap width, and would be doubled by a similar relative decrease in the gap width. Thus, in order to avoid significant reflection as the gap width changes a much faster relative decrease in gap width can be tolerated near the top...
of the groove, where the gap is wide, compared with near the bottom, where the gap is narrow. Furthermore, since the gap-SPP propagation length for extremely narrow gap-widths becomes proportional to the gap-width it is also favourable to have as long a length as possible where the gap is narrow. With these considerations in mind we expect that in order to increase the absorption, and thus to reduce the reflectivity, when the maximum groove depth is restricted, we should use a geometry such as the one in figure 1(a) with a smallest possible bottom groove width $\delta$ and bottom groove angle $\alpha$. With such a geometry the gap-SPP absorption per unit propagation length will be extremely high near the groove bottom, and, since the groove walls are practically parallel there, the high absorption will also occur over a distance that is much larger than the one found in e.g. a V-groove. At the same time, with this geometry the groove is narrowing fast near the top, where this will not have a large effect on the propagation constant of the gap-SPP wave, and slowly near the bottom, where the effect of the gap-width on the propagation constant is much larger.

The above qualitative considerations regarding the tapering of grooves can be made quantitative by taking a closer look at how the gap-SPP mode index depends on the gap-width. The gap-SPP mode index defined as the ratio of gap-SPP propagation constant $k_{\text{gap-SPP}}$ to the free-space wave number $k_0$ is shown in figure 2 versus the width of the air-gap $w$ between two gold surfaces for two wavelengths of 600 and 800 nm. The exact gap-SPP mode index calculated with a transfer-matrix method (see e.g. [27]) is shown with solid lines, i.e. black solid line for the wavelength 600 nm and red solid line for the wavelength 800 nm. The dashed lines correspond to the following approximation to the mode-index being valid in the limit of extremely small air-gap widths [28]:

$$n_{\text{gap-SPP, app. 1}} = \frac{\lambda_0}{\pi w (-\varepsilon_m)}, \quad (1)$$

where $\lambda_0$ is the free-space wavelength, and $\varepsilon_m$ is the corresponding metal dielectric constant. It can be seen from figure 2 that this approximation works quite well for gap widths smaller
than 1–2 nm. The dotted lines correspond to the following approximation to the mode-index being valid for an intermediate region with \( w > \lambda_0 / (-\pi \varepsilon_m) \) corresponding to \( w > 20.2 \text{ nm} \) for \( \lambda_0 = 600 \text{ nm} \), and \( w > 10.6 \text{ nm} \) for \( \lambda_0 = 800 \text{ nm} \) [28]:

\[
n_{\text{gap-SPP, app, 2}} = \sqrt{1 + \frac{\lambda_0 \sqrt{1 - \varepsilon_m}}{\pi w (-\varepsilon_m)}},
\]

which is also shown in figure 2 where it works reasonably well for the appropriate widths.

The adiabatic transition requirement equivalent to requiring that the gap-SPP mode-effective index over the distance of one gap-SPP wavelength along the z-axis should be small can be formulated [29, 30]:

\[
\frac{d}{dz} \left( \frac{1}{k'_{\text{gap-SPP}}} \right) = \frac{\lambda_0}{2\pi} \left[ n'_{\text{gap-SPP}} \right]^2 \frac{d}{dw} \left( \frac{dw}{dz} \right) \ll 1,
\]

where the prime means that we should use only the real part of the mode-index or propagation constant. The groove half-tapering angle \( \alpha \) at a specific depth \( z \) is directly related to the change in groove width per unit depth change resulting in the following requirement to the half-tapering angle:

\[
\alpha(w, \lambda_0) \ll \tan^{-1} \left( \frac{\pi}{\lambda_0} \left[ n_{\text{gap-SPP}} \right]^2 \frac{d}{dw} \left( \frac{dw}{dz} \right) \right) = \beta(w, \lambda_0).
\]

We have plotted an exact calculation of the limiting angle \( \beta \) (obtained from equation (4) and the data in figure 2(a)) in figure 3 considering the wavelength 800 nm. It is clear that when the groove width is large a much larger tapering angle can be tolerated compared with the case.
of a small groove width. We also notice that in the limit of extremely small groove widths the limiting angle $\beta$ reaches a constant value. This can be understood by inserting equation (1) into equation (4) (Approximation 1), in which case the constant value reached in figure 3 is directly calculated. The approximation to the limiting angle that will be reached when inserting equation (2) into equation (4), and neglecting the imaginary part of $\varepsilon_m$, is also shown in figure 3 (Approximation 2). This approximation is seen to work extremely well for the whole range of considered widths and practically coincides with the exact calculation. It is clear from figure 3 that the requirement equation (4) is only satisfied near the groove bottom for nearly parallel groove walls, and thus ultra-sharp grooves are required.

3. V-grooves and power-formula grooves

In this section we will study reflectivity spectra for periodic arrays of V-grooves and power-formula grooves. While such grooves are sharp they are, however, not ultra-sharp and do not satisfy the tapering requirements for different depths discussed in section 2. When the results are later compared with results for ultra-sharp groove geometries that do satisfy those tapering requirements it will become clear that the reflectivity levels are quite different.

A periodic array of V-grooves can be obtained from the geometry in figure 1(a) by choosing an appropriate bottom groove angle $\alpha$ that we shall refer to as $\alpha_V$. With this choice of angle the parts of circles governing the main part of the groove surfaces will become straight lines corresponding to an infinite radius of curvature. We have chosen a relatively small top flat section of width $a = 10 \text{ nm}$ and curvature for the corners near the top of grooves of $r = 10 \text{ nm}$ similar to what is used later for ultra sharp groove geometries. We also consider a period of $\Lambda = 250 \text{ nm}$ being small enough that higher reflection diffraction orders are not allowed for the considered wavelengths (450–850 nm) for angles of light incidence up to $\sin^{-1} \left( \frac{450}{250} - 1 \right) = 53^\circ$, and we consider $y$ polarized normally incident light (see figure 1). The reflectivity spectra presented in this paper include all reflected waves and not only specularly reflected light.

For a fixed groove depth $H = 500 \text{ nm}$ we have studied the effect of a decreasing bottom width $\delta$ at the bottom rounding point (figure 4(a)) considering bottom groove widths ranging from 50 to 0.3 nm. Clearly, the overall reflectivity decreases with decreasing bottom width $\delta$ but not very fast. Even for the smallest realistic groove width of 0.3 nm corresponding approximately to the width of a gold atom the reflectivity for the longer considered wavelengths is significant. For this smallest bottom groove width we have then investigated the effect of increasing the groove depth $H$ further (figure 4(b)) considering groove depths from 500 to 1000 nm. It is observed that increasing the groove depth also tends to decrease the reflectivity but also here the reflectivity decrease does not occur very fast with the increasing groove depth. In figure 4(b) we have also shown the corresponding reflectivity spectrum for a perfectly flat gold surface, and for the longer wavelengths even the groove depth of 1000 nm for the smallest bottom width of 0.3 nm does not decrease the gold surface reflectivity by more than approx. a factor of 2. Note that as the depth $H$ increases in figure 4(b) the reflectivity spectra show an increasing number of small oscillations that can be related to standing-wave gap-plasmon-polariton resonances similar to our previous work on V-grooves [21, 31], and similar to [32].

It is clear from the data in figure 4 that there is a relatively sharp transition in the reflectivity around wavelengths of approx. 600 nm, where the reflectivity level changes from being very small to being large, which is a consequence of the metal (gold) becoming less absorptive.
Figure 4. Reflectivity spectra for periodic arrays of V-grooves corresponding to the geometry in figure 1(a) with parameters \( r = a = 10 \) nm, \( \Lambda = 250 \) nm, and normally incident \( y \)-polarized light \( (\theta = 0) \). (a) Calculation of the effect of a decreasing bottom width \( \delta \) for a fixed groove depth \( H = 500 \) nm. (b) Calculation of the effect of an increasing groove depth \( H \) for a fixed bottom width \( \delta = 0.3 \) nm. Also shown is the reflectivity for a flat gold surface.

Figure 5. Reflectivity spectra for periodic arrays of grooves in a gold surface where the surface follows a power formula corresponding to the geometry in figure 1(b) and normally incident \( y \)-polarized light. (a) Case of a parabolic surface \( (N = 2) \) and bottom groove width \( \delta = 0.3 \) nm considering a range of groove depths \( H \). (b) Considering an increase of the power number \( N \) for both a very small bottom width \( \delta = 0.3 \) nm and a larger bottom width \( \delta = 10 \) nm. Fixed groove depth \( H = 500 \) nm. A few of the considered geometries are shown as an inset.

for the longer wavelengths. A similar transition was seen in a previous work on periodically nanostructured metallic surfaces combining gold and PMMA ridges [34].

As an alternative to V-grooves we shall now consider sharper geometries corresponding to the surfaces in figure 1(b) with \( N > 1 \). Reflectivity spectra for the case of parabolic surfaces \( (N = 2) \) is studied in figure 5(a) for a bottom groove width \( \delta = 0.3 \) nm, period \( \Lambda = 250 \) nm, and a range of groove depths \( H \) from 500 to 1000 nm. A general decrease in reflectivity with

New Journal of Physics 15 (2013) 013034 (http://www.njp.org/)
increasing groove depth $H$ is observed but the reflectivity is only a little bit lower for the same depths compared with the case of V-grooves and the same bottom groove width (figure 4(b)). We also notice that the number of oscillations related to standing wave interference of counter-propagating gap-SPP waves in the grooves increases with increasing groove depth.

Surfaces where the power number $N$ is increased further are considered in figure 5(b) for a small $\delta = 0.3$ nm and a larger bottom width $\delta = 10$ nm. We notice that increasing the power number $N$ can decrease the reflectivity for some of the longer wavelengths but not dramatically, and at the same time the reflectivity is increased for the shorter wavelengths. As $N$ increases the geometry becomes more flat near the top which can explain the increasing reflectivity with $N$ for the shorter wavelengths.

4. Ultra-sharp grooves

In this section we will consider reflectivity spectra for ultra-sharp grooves. We will show that in the limit of adiabatic nanofocusing, i.e. the limit where the gap taper angle for different widths is much smaller than the limiting angle in figure 3, the reflectivity levels are profoundly smaller compared with the other considered geometries (section 3) that are not satisfying this condition.

The first geometry we will consider is obtained by simply choosing a groove tapering angle $\alpha$ at each position along the groove $z$, or equivalently for each groove width obtained along the groove, as the limiting angle $\beta$ in figure 3 divided by a factor being larger than unity. At the top of the grooves the geometry starts with part of a small circle for the first few nanometres to arrive at the appropriate starting groove taper angle. When the groove width is tapered down to the width $\delta$ the groove bottom is rounded off with part of a circle. Having specified the period $\Lambda$ and the bottom groove width $\delta$ the desired groove depth can be obtained by tuning the angle division factor. The reflectivity spectra for such grooves considering a range of bottom groove widths $\delta$ for a fixed groove depth $H = 500$ nm are presented in figure 6(a). Here the angle division factor is approx. 3.13 [$\alpha(w) = \beta(w)/3.13$] when $\delta = 0.3$ nm and 6.35 when $\delta = 50$ nm. Calculations for a fixed bottom groove width $\delta = 0.3$ nm and a range of groove depths $H$ are presented in figure 6(b). The result for the groove depth $H = 111$ nm corresponds to a situation where the taper angle $\alpha(w) = \beta(w)$, and thus for the other considered depths $H$ we have $\alpha(w) < \beta(w)$. It is possible to have very efficient resonant absorption for certain wavelengths even with a very small groove depth $H = 111$ nm. A similar result has previously been obtained by Perchec for rectangular grooves [33]. However, low reflectivity for a broad range of wavelengths is only obtained when the bottom groove width $\delta$ is ultra-small and when the groove depth is sufficiently large at the same time.

The general considerations in section 2 suggested that it might be even better for broadband absorption of light to use a bottom groove angle $\alpha$ that is zero rather than some fraction of $\beta$. We have presented results for such a geometry (figure 1(a) with groove depth $H = 500$ nm) in figure 7 considering either a bottom taper angle $\alpha = 0$ and varying bottom groove width $\delta$ (figure 7(a)) or a fixed bottom groove width $\delta = 0.3$ or 10 nm and a varying bottom groove angle $\alpha$ considering the transition from V-grooves ($\alpha = \alpha_V$) to ultra-sharp grooves $\alpha = 0$.

It is clearly seen that when the bottom taper angle $\alpha = 0$ the reflectivity decreases dramatically when the bottom groove width becomes ultra-small. Theoretical calculations with even smaller bottom groove widths and local response theory results in even smaller reflectivities. However, we think that the value of $\delta = 0.3$ nm is the smallest bottom groove width that we can consider in the calculations since this width is approximately the size of

New Journal of Physics 15 (2013) 013034 (http://www.njp.org/)
Figure 6. Reflectivity spectra for periodic arrays of grooves obtained by requiring that the groove taper angle is given by the angle in figure 3 (exact result) divided by a factor. The groove depth $H$ is controlled by this factor. The groove bottom is rounded off with part of a circle when the groove width reaches the width $\delta$. The top of the groove starts with part of a circle within the first two nanometers leading up to the desired starting groove inclination angle. The period is $\Lambda = 250 \text{ nm}$, and the spectra are for normally incident $y$-polarized light ($\theta = 0$). (a) Calculations for a fixed groove depth $H = 500 \text{ nm}$, and a range of bottom groove widths $\delta$. (b) Calculations for a fixed bottom groove width $\delta = 0.3 \text{ nm}$, and a range of groove depths $H$.

Figure 7. Reflectivity spectra for periodic arrays of grooves in a gold surface corresponding to the geometry in figure 1(a) with $\Lambda = 250 \text{ nm}$, $H = 500 \text{ nm}$, $a = r = 10 \text{ nm}$, and normally incident $y$-polarized light. (a) For a fixed bottom groove angle $\alpha = 0$ the transition from a wide bottom groove width $\delta = 50 \text{ nm}$ to a small bottom groove width $\delta = 0.3 \text{ nm}$ is considered. (b) For a fixed bottom groove width of $\delta = 0.3$ or 10 nm the transition from a large bottom groove angle equivalent to a V-groove ($\alpha = \alpha_V$) to ultra sharp grooves with $\alpha = 0$ is considered.

a gold atom. The transition to the adiabatic nanofocusing limit is considered in another way in figure 7(b), where here it is the bottom groove width that is held fixed at either $\delta = 0.3$ or 10 nm while the bottom groove angle $\alpha$ is reduced from that corresponding to a V-groove.
Figure 8. Calculation of the effect of increasing the groove depth $H$ for a geometry (figure 1(a)) characterized by the parameters $a = r = 10$ nm, $\delta = 0.3$ nm, $\Lambda = 250$ nm, $\alpha = 0$, and normally incident ($\theta = 0$) light. (a) $y$ polarized incident light. (b) $x$ polarized incident light.

($\alpha = \alpha_V$) to that of ultra sharp grooves ($\alpha = 0$). It is clearly seen that for the smallest bottom groove width of $\delta = 0.3$ nm the reflectivity again dramatically decreases as the bottom groove angle is reduced towards $\alpha = 0$. A similar reduction in reflectivity is not seen when the bottom groove width $\delta = 10$ nm. The results for the two different kinds of ultra-sharp groove geometries (figures 6 and 7) are quite similar but perhaps the latter geometry (figure 1(a) with $\alpha = 0$) offers slightly smaller reflectivity levels. For the rest of this section we will consider the geometry in figure 1(a).

The effect of a further increase of groove depth but considering smaller steps is illustrated in figure 8(a). It is clearly possible to further decrease the reflectivity to any desired low reflectivity level by increasing the depth of grooves. It is also seen that a change in depth of only 50 nm is sufficient to approximately replace a reflectivity peak with a reflectivity dip. Thus, while there are many oscillations in the theoretical reflectivity spectra related to standing-wave interference of counter-propagating gap-SPPs then in an experiment, where the groove depth might vary a little bit from one groove to the next, these oscillations will average out. In a similar way small changes in the bottom groove width shift reflectivity peaks and dips and also lead to an averaging out of oscillations in spectra. This can explain the absence of the oscillations in experimental results [17]. A similar calculation but for $x$ polarized light is shown in figure 8(b). Here we notice that increasing $H$ only helps marginally to reduce the reflectivity, and the reflectivity levels are much higher here. It is not possible to excite gap-SPP waves for this polarization, and thus the mechanism responsible for high absorption in figure 8(a) is absent.

So far we have only considered normally incident light. However, in a practical experimental measurement the focusing of light onto the possibly small sample leads to light incident under a range of angles at the same time. Here we investigate theoretically (figure 9) how changing the angle of light incidence will affect the reflectivity spectra. For our ultra-sharp geometry (figure 1(a) with $a = r = 10$ nm, $\delta = 0.3$ nm, $\Lambda = 250$ nm, $H = 500$ nm, and $\alpha = 0$) we find for $p$ polarized incident light (figure 9(a)) that the reflectivity spectra are only marginally different for the angles of incidence $\theta = 0^\circ$ and $20^\circ$. This is in agreement with the prediction in [32] that reflection minima for zero-order gratings (no propagating higher reflection–diffraction orders) would be fairly insensitive to the angle of light incidence.
Figure 9. Calculation of the effect of increasing the angle of light incidence $\theta$ on total-reflectivity spectra. The light is propagating in the $yz$ plane. (a), (c) The electric field is polarized in the $yz$ plane ($p$ pol.). (b), (c) The electric field is polarized along the $x$-axis ($s$ pol.). (a), (b) The light is incident on the periodic groove array in figure 1(a) with $a = r = 10 \text{ nm}$, $\delta = 0.3 \text{ nm}$, $\Lambda = 250 \text{ nm}$, $H = 500 \text{ nm}$, and $\alpha = 0$. (c), (d) Light is incident on a perfectly flat gold surface. For $\theta = 40^\circ$ the reflectivity level is still small but peaks in reflectivity spectra are shifted in wavelength. Further increasing the angle of light incidence leads to an increasing reflectivity level. It appears that as long as the angle of light incidence is not larger than $\theta = 40^\circ$ the low reflectivity level is not much affected by having a different angle of incidence. Thus a significant amount of focusing is possible without increasing the measured reflectivity. A similar calculation but for $s$ polarized light is shown in figure 9(b). Here the reflectivity increases with the increasing angle of incidence. For this polarization the surface is clearly not black due to the high reflectivity levels. Reflectivity spectra versus angle of incidence for a flat gold surface are shown in figure 9(c) for $p$ polarization and in figure 9(d) for $s$ polarization for comparison. Notice that there is a non-zero angle of light incidence that gives a minimum reflectivity for $p$ polarization similar to the Brewster angle for dielectric materials.

We found already for the power-formula surfaces (figure 1(b)) that as the grooves became sharper, but the top parts of the geometry would also become more flat, the reflectivity level could increase, especially for the shorter of the considered wavelengths (figure 5(b)). For the ultra sharp groove geometry (figure 1(a)) it is also possible to increase the width of a flat
Figure 10. (a) Calculation of the effect of a plateau of varying width \(a\) on the reflectivity spectra for \(y\) polarized light being normally incident on the ultra sharp groove geometry (figure 1(a)) with \(r = 2\ \text{nm}, H = 500\ \text{nm}, \Lambda = 250\ \text{nm}\), and \(\alpha = 0\). (b) Similar calculations but with \(\Lambda = 250\ \text{nm} + a\).

plateau at the top part between grooves by adjusting the parameter \(a\). In an experimental fabrication of black gold surfaces such a plateau can also be present [17]. Here we consider in figure 10(a) reflectivity spectra for the ultra-sharp black gold geometry (figure 1(a), \(r = 2\ \text{nm}, \delta = 0.3\ \text{nm}, \alpha = 0, H = 500\ \text{nm}, \Lambda = 250\ \text{nm}\)) with an increasing top flat part of width \(a\). We clearly notice that for widths \(a = 0\) or 40 nm the reflectivity levels are not much different but the reflectivity peaks and minima are noticeably shifted. For \(a = 40\ \text{nm}\) the short-wavelength reflectivity is more than doubled but it is still very small. As the width \(a\) increases further the reflectivity, especially for the shorter wavelengths, starts to increase more rapidly. However, overall quite large plateau widths can be tolerated without serious degradation of the blackness (low reflectivity) of the structured gold surface. Notice that if the plateau is varying on an experimental sample the shifts in peaks and minima will also lead to their averaging out in an experimental reflectivity measurement. A similar effect as seen in figure 10(a) with increasing \(a\) can be obtained by instead increasing \(r\) (not shown). In figure 10(b) we consider increasing both the width of the flat plateau and the period at the same time such that shape of grooves is unchanged. In this case the wavelengths of reflectivity peaks and minima are only weakly affected by the width of the plateau. The large changes in wavelengths of reflectivity minima in figure 10(a) with the plateau width is thus mainly due to the resulting change in the groove shape.

From a fabrication point of view it might be desirable to use a larger period than 250 nm. However, for periods that are twice as large or more there will even for normally incident light be diffraction effects for some of the considered wavelengths, resulting in higher total reflection. This is shown in figure 11 where we consider reflectivity spectra for the ultra sharp groove geometry (figure 1(a), \(\delta = 0.3\ \text{nm}\) and \(\alpha = 0\)) but with larger periods of \(\Lambda = 500\) or 750 nm for normally incident \(y\) polarized light, and a groove depth kept at \(H = 500\ \text{nm}\) as considered previously, and another groove depth of 1000 or 1500 nm in order to have grooves with the same shape as considered previously for \(\Lambda = 250\ \text{nm}\). Notice that the total reflectivity increases markedly as the wavelength becomes smaller than the period. This is because of the presence of higher reflection diffraction orders and therefore additional available reflection channels. If the groove depth is kept at \(H = 500\ \text{nm}\) the reflectivity for the increased period compared with
Figure 11. Total-reflectivity spectra for ultra-sharp periodic arrays of grooves in a gold surface (figure 1(a), $r = a = 10 \text{ nm}$, $\delta = 0.3 \text{ nm}$ and $\alpha = 0$) for normally incident $y$ polarized light and different groove depths $H$ and periods $\Lambda$.

Figure 12. Reflectivity spectra for $y$-polarized light being normally incident on ultra sharp periodic groove arrays (figure 1(a)) with $a = 0$, $H = 120 \text{ nm}$, $\Lambda = 50 \text{ nm}$, $\delta = 0.3 \text{ nm}$, and $r = 2 \text{ nm}$ for bottom groove angles from that of a V-groove ($\alpha = \alpha_V$) to $\alpha = 0$.

previous results ($\Lambda = 250 \text{ nm}$) and the same groove depth is generally increased (compare e.g. with figure 7).

For an increased depth at the same time to keep the groove shape unchanged compared with the case of period 250 nm and depth 500 nm the reflectivity is clearly smaller for wavelengths that are larger than the period, i.e. when there are no higher reflection diffraction orders available. But for the smaller wavelengths this is reversed and the reflectivity is comparably larger instead.
Instead of considering the effect of a larger period and depth we can also investigate if we can still use the adiabatic nanofocusing effect if we decrease both the period and depth dramatically such that the shape of grooves is approximately unchanged. In figure 12 we consider again reflectivity spectra for \( y \) polarized light being normally incident on the ultra-sharp groove geometry (figure 1(a)) with \( r = 2 \) nm, \( a = 0 \), \( \delta = 0.3 \) nm, \( \alpha = 0 \). One significant drawback when just scaling down the geometry is that it is not possible to scale down the smallest possible groove width at the bottom of the groove to a value smaller than the size of a gold atom. Therefore, in the calculations in figure 12 this width was maintained at \( \delta = 0.3 \) nm. Clearly, the reflectivity levels are markedly higher compared with the ultra-sharp groove reflectivities shown in figures 6 and 7 for the period 250 nm and groove depth 500 nm. It is seen though that with this design the reflectivity can be very small for specific wavelengths even though the period and depth are quite small, which is another example of an absorption resonance similar to the one found in [33]. Note that the scaled down geometry only satisfies equation (4) at the very bottom of the groove.

Since gold is an expensive material we may want to consider if it is possible to obtain the same absorption of light with a structured thin gold film rather than making a surface structure in a much thicker planar gold film of thickness \( > 500 \) nm. We have considered this situation in figure 13 for a thin gold film where the upper surface is structured in the same way as in the case of ultra-sharp grooves considered previously (figure 1(a), \( r = a = 10 \) nm, \( \delta = 0.3 \) nm, \( \alpha = 0 \), \( H = 500 \) nm, \( \Lambda = 250 \) nm), and with a lower surface constructed to give a film-thickness of approx. 30, 40 or 50 nm (see inset in (a)). The reflection for the case of infinite film thickness is shown for comparison.

Figure 13. Theoretical reflection spectra (a) and transmission spectra (b) for a periodic gold thin-film geometry with an upper surface matching the periodic ultra-sharp groove geometry (figure 1(a), \( r = a = 10 \) nm, \( \delta = 0.3 \) nm, \( \alpha = 0 \), \( H = 500 \) nm, \( \Lambda = 250 \) nm) and with a lower surface constructed to give a film-thickness of approx. 30, 40 or 50 nm (see inset in (a)). The reflection for the case of infinite film thickness is shown for comparison.
smaller when the film thickness is finite we find for the considered film thicknesses that there is a transmission (figure 13(b)) that can easily be larger than the reflection. We need here a film thickness on the order of 100 nm to effectively eliminate the transmission.

5. Using another metal: silver, chromium, platinum and palladium

In this section we will study reflectivity spectra for periodic arrays of ultra sharp grooves in silver, chromium, platinum, nickel and palladium. Compared with gold these metals are either less lossy (silver) or more lossy (chromium, platinum, nickel and palladium). The blackness of the structured metal surfaces considered in this paper are all related to absorption of light by the metal since there will be no transmission through the metal, and all light that is not absorbed must be reflected. Thus, we can expect that the more lossy a metal is the easier it is to obtain a black surface by microstructuring, and the less lossy a metal is the less black such a surface will be.

Silver is less lossy than gold, especially for the shorter of the visible wavelengths considered, and thus we expect that it is more difficult to make a black structured silver surface compared with gold. This is illustrated with the calculations in figure 14 showing a comparison between reflection spectra for a periodic ultra-sharp groove geometry (figure 1(a), \( r = a = 10 \text{ nm}, \delta = 0.3 \text{ nm}, \alpha = 0, H = 500 \text{ nm}, \Lambda = 250 \text{ nm} \)) using both gold and silver. Clearly, the reflection is much higher for silver compared with gold. Thus, creating a black silver surface is a much tougher challenge than creating a black gold surface. For comparison is also shown reflectivity spectra for flat gold and silver surfaces.

The metals chromium (Cr), nickel (Ni), platinum (Pt) and palladium (Pd) are all significantly more lossy than gold for all the considered wavelengths. Therefore, we will show...
Figure 15. Theoretical reflectivity spectra for the periodic ultra-sharp convex groove (figure 1(a), \( r = a = \delta = 10 \text{ nm}, \alpha = 0, H = 500 \text{ nm}, \) and \( \Lambda = 250 \text{ nm} \)) in different metals for normally incident (a) \( y \) polarized light, and (b) \( x \) polarized light. (c) Reflectivity spectra for corresponding flat metal surfaces.

that the criteria of an ultra-small bottom groove width can be relaxed a bit while retaining a black microstructured surface.

Reflectivity spectra for periodic ultra-sharp groove arrays in these metals for normally incident \( y \) polarized light (figure 1(a), \( r = a = 10 \text{ nm}, \alpha = 0, H = 500 \text{ nm}, \) and \( \Lambda = 250 \text{ nm} \)) with the bottom groove width set to \( \delta = 10 \text{ nm} \) are shown in figure 15(a). For the considered wavelengths the highest reflectivity is approx. 6\% for palladium, approx. 3\% for platinum, and approx. 1\% for chromium. Clearly, these reflectivities are much smaller than those found for gold despite that the bottom groove width is much larger. Thus it will be much easier to make e.g. a black nickel or black palladium surface by microstructuring. The bottom groove width of \( \delta = 10 \text{ nm} \) is even within reach of what can be fabricated with nanoimprint lithography and reactive ion-etching \[35\]. For comparison we have shown a similar calculation but for \( x \) polarized incident light (figure 15(b)) and for flat metal surfaces (figure 15(c)).
6. Conclusion

In this paper we have quantified how to taper grooves in a metal surface, in order to make the best of a limited groove depth, such that gap-SPP waves propagating in the grooves towards the groove bottom will experience small reflection. By requiring that the change in the gap-SPP mode index must be small over a distance of a gap-SPP wavelength it was found that a much larger tapering angle can be tolerated near the top of the groove, where it is wide, compared with near the bottom of the groove, where it is narrow. Near the bottom of grooves the groove walls must be nearly parallel, and thus grooves must be ultra-sharp.

It was exemplified for structures that do not satisfy this tapering principle, namely for V-grooves and grooves described by a power-formula, that it is not possible to obtain a very small reflectivity, since these grooves are not sufficiently sharp near the groove bottom. It was demonstrated that ultra-sharp groove arrays behave quite differently having much smaller reflectivity over a broad range of wavelengths, and to an extent that such surfaces can be considered as black surfaces. Some oscillations with wavelength were observed in theoretical reflectivity spectra even though such oscillations are absent in experimental reflectivity spectra [17]. This can be explained by observing that the theoretical structures are perfectly periodic structures, while some variation can be expected from one groove to the next in the experimental structures. The oscillations in the theoretical calculations were found to be sensitive to e.g. the exact groove depth, the width of a plateau near the top of the grooves, the angle of light incidence, etc, and thus, the superposed reflectivity spectra from many slightly different situations will average out the oscillations in the reflectivity spectra.

It was shown that if periodic groove arrays are made in a silver surface instead then the reflectivity is much higher compared with gold, while it can be much smaller if chromium, nickel, platinum or palladium are used, as a consequence of silver being less absorptive than gold, and the other metals being more absorptive than gold. For the latter more absorptive metals the ultra-sharpness of the groove near the groove bottom can be relaxed to an extent that fabrication of the surface structure using nanoimprint lithography and reactive-ion etching is within reach.

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New Journal of Physics 15 (2013) 013034 (http://www.njp.org/)
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