Mie plasmon enhanced diffraction of light from nanoporous metal surfaces

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Abstract: The diffractive properties of gold films with a periodic lattice of sub-micron voids beneath the surface are investigated. It has been shown that nanoporous metal surfaces exhibit *frequency-selective non-dispersive diffraction* enhanced by Mie plasmons in nanovoids, which leads to *absolute angular tolerance* of the diffracted beam intensity that can be useful for a variety of applications covering angle-tolerant optical filters, deflectors, absorbers, and beam splitters. Diffraction spectra are measured and calculated to support these conclusions, showing good qualitative agreement.

OCIS codes: (050.1950) Diffraction gratings; (240.6680) Surface plasmons; (290.4020) Mie theory; (290.4210) Multiple scattering; (160.3900) Metals

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The optical properties of metallic gratings have been the subject of extensive research for over a century. One of the early achievements of the optics of metal gratings was the discovery and understanding of the Wood anomalies [1] in the reflection spectra, which have been assigned later into two types. One type of anomaly is caused by excitation of surface plasmon-polaritons propagating on the planar metal surface. Another type is the diffractive anomaly which is associated with the opening of new diffraction orders into surrounding media (also called Rayleigh anomalies). Considerable advances in assembly of microporous and nanoporous metal structures [2, 3, 4, 5] have prompted the investigation of their optical properties and renewed the interest in these problems. A lattice of voids beneath the metal surface can act as a coupling element, which couples incoming light to the surface plasmon-polaritons and diffracted beams. In this specific type of resonant grating coupler, the inherent confined resonances in the voids (Mie plasmon resonances) can be excited. Therefore, one can expect a complex optical response associated with different types of plasmon excitations in the periodic porous metal structures. The role of surface plasmon-polaritons and Mie plasmons in molding reflection, transmission, and absorption spectra has been discussed in recent publications [6, 7, 8, 9]. In particular, remarkable effects of extraordinary transmission [6] and absorption [7] caused by excitation of Mie plasmons in nanopores (localized void plasmons) have been predicted. The interaction between surface-plasmon polaritons and Mie plasmons localized in buried voids has been observed in reflectivity spectra of nanoporous metal surfaces in [8] and theoretically explained in [9]. However, the interaction between diffracted beams and Mie plasmons on the surface of nanoporous metal has not been studied either experimentally or theoretically.

Rayleigh anomalies become more pronounced when resonances such as surface plasmons are involved [10]. However, a periodic corrugation of the metal surface is needed to excite the surface plasmons. In this case, both the surface corrugation symmetry and the surface plasmon dispersion relation are important to determine the frequencies for strongest plasmonic response, which become very sensitive to incident beam tilt angles. The lack of angular tolerance prevents practical applications of these structures as guided-modes resonant grating filters [11, 12]. This is also the case for localized plasmons in metallic particles arranged in periodic lattices, where pronounced dispersion effects due to inter-particle interaction take place [13]. In contrast to that, plasmons in voids are so strongly localized [2, 9] that even when the voids are arranged in close-packed lattices the coupling through the metal between voids is weak and they appear as nearly dispersionless resonances [2, 9].

In this paper we show that nanoporous metal surfaces exhibit *frequency selective diffraction* enhanced by Mie plasmons in nanovoids, which leads to *absolute angular tolerance* of the diffracted beam intensity that can be useful for a variety of applications ranging from angle-tolerant optical filters, deflectors, absorbers, and beam splitters. We study the plasmonic and photonic properties of a hexagonal two-dimensional ($2D$) lattice of spherical nanovoids buried below a planar metal surface (Fig. 1) both experimentally and theoretically.

The experimental sample of nanoporous gold was prepared using a nanoscale casting technique with electrochemical deposition of metal through a self-assembled latex template. Templates were produced using a capillary force method, by which the latex spheres were initially deposited onto a gold-coated glass slide from colloidal solution, allowing a monolayer of well-ordered spheres to be produced. Electrodeposition, while measuring the total charge passed, allows the accurate growth of metal to a required thickness t. The resulting metallic mesh reflects the order of the self-assembled close-packed template, allowing convenient control of the pore diameters and regularity of the array. After deposition the template is dissolved, leaving the free-standing structure. This allows the production of shallow well-spaced dishes as well as nearly encapsulated spherical voids on a single sample. Optical and electron microscopy shows that the resulting surfaces are smooth on the sub-10 nm scale. The sub-3% size dispersion of the latex spheres results in an identical size dispersion of voids, while detailed diffraction measurements confirm the single-domain nature of the samples. The detailed description of the technique is given elsewhere [14, 15].

To calculate the optical spectra of a nanoporous metal surface we use a self-consistent electromagnetic multiple-scattering layer-Korringa-Kohn-Rostoker (KKR) approach [6, 7, 16, 17] that makes use of a re-expansion of the plane-wave representation of the electromagnetic field in terms of spherical harmonics. This approach involves the following steps. First, we divide the whole structure into parts separated by parallel planes that form two homogeneous semi-infinite media and a planar layer in between that contains the periodic lattice of voids or spheres. The semi-infinite medium below the periodic layer is a homogeneous metal, while the homogeneous semi-infinite medium above the periodic layer is vacuum. The periodically structured layer is treated within the KKR method in a spherical-wave representation, whereas the interaction between the field in the periodic layer and the field in the homogeneous semispaces is treated separately in a plane-wave representation. We describe the dielectric function of gold $\varepsilon(\omega)$ by optical experimental data [18]. Our electromagnetic approach allows us to elucidate the interaction of localized Mie plasmons in voids, delocalized surface plasmon-polaritons, and diffracted photons. We focus here on the effect of Mie plasmons on the diffracted photon beams originating in the opening of new diffraction channels (which are projected as the Rayleigh anomalies in the specular reflection spectra). Mie plasmon resonances are shown to result in strong features in the non-specular diffracted beam spectra, where both theory and experiment exhibit good qualitative agreement.

Let us consider light incident at an angle θ to the surface normal, upon a planar surface of metal that contains a $2D$ hexagonal lattice of voids with primitive vectors $\mathbf{a}$ and $\mathbf{b}$ ($|\mathbf{a}| = |\mathbf{b}|$)

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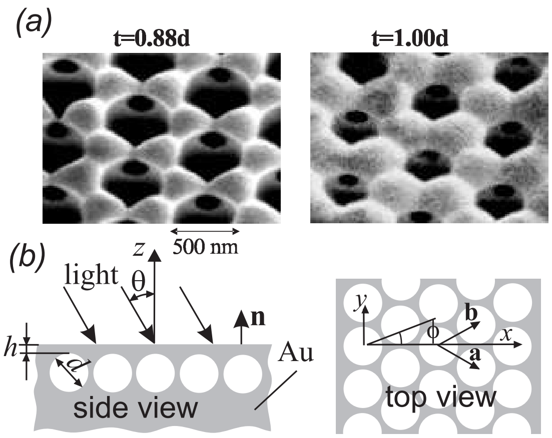

Fig. 1. (a) SEM image of nanoporous metal structure with close-packed void lattice grown up to a thickness t (b) the theoretical model of nanoporous metal surface with a $2D$ hexagonal lattice of spherical voids.

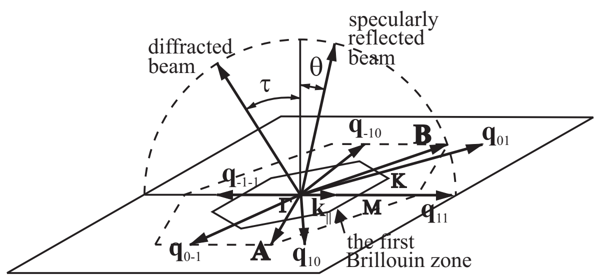

Fig. 2. The first Brillouin zone and the photons wavevectors. Plane of incidence is along $\Gamma - M$ direction.

just beneath the surface. The plane of incidence of external light is defined by the azimuthal angle ϕ measured with respect to the x-axis (Fig. 1b).

The diffracted beams emerge at the frequencies of the grazing photons, which can be estimated in the 'empty lattice approximation' as

$$\omega = c|\mathbf{q}_{pq}|, \tag{1}$$

where $\mathbf{q}_{pq} = \mathbf{k}_{\|} + \mathbf{g}_{pq}$, $\mathbf{g}_{pq} = p\mathbf{A} + q\mathbf{B}$ are reciprocal void-lattice vectors, $\mathbf{A}$ and $\mathbf{B}$ are the primitive vectors of the reciprocal $2D$ void lattice (Fig. 2), p and q are integers, and $k_{\|} = (\omega \sin\theta)/c$ is the in-plane component of the incident light wavevector, which is equal to zero in the case of normal incidence. Note that the frequencies of grazing photons are close to (they fall just below) the frequencies of surface plasmon-polaritons [9],

$$|\mathbf{q}_{pq}|^2 = (\omega/c)^2(\omega^2 - \omega_p^2)/(2\omega^2 - \omega_p^2), \tag{2}$$

where ω_p is the free electron plasma frequency, in high-conductivity metals (when $\omega_p >> \omega$).

The frequencies of void plasmons can be estimated in the framework of a simple model of plasmon modes supported by a spherical void in an infinite metallic medium [2]:

$$h_l^{(1)}(\rho_0)[\rho_1 j_l(\rho_1)]' = \varepsilon(\omega) j_l(\rho_1)[\rho_0 h_l^{(1)}(\rho_0)]', \tag{3}$$

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where $\rho_0 = \omega r\sqrt{\varepsilon(\omega)}/c$, $\rho_1 = \omega r/c$, r is the radius of the void, $j_l(x)$ is a spherical Bessel function of the first kind of l-th order (l is the orbital momentum quantum number), $h_l^{(1)}(x)$ is a spherical Hankel functions of the first kind, and the prime denotes differentiation with respect to the argument.

Figure 3(a) shows the measured intensity of the zero-order reflected beam (specular reflection spectrum) as a function of photon energy $\hbar\omega$ and angle of incidence θ for a nanoporous gold surface formed by the periodic arrangement of close-packed spherical nanovoids (with $d =$ 500 nm) grown up to the void diameter $t = d$ (Fig. 1a). Note that there are residual void openings and interconnection of voids in the sample, which are not described by our theoretical model, although their effect seems to lie more in the details than in the qualitative optical response. The incident light has p-polarization with its plane of incidence along the $\Gamma - M$ direction of the first Brillouin zone (see Fig. 2), which corresponds to zero azimuthal angle ($\phi = 0$). Calculations (Fig. 3b) are performed for a single $2D$ hexagonal lattice ($|\mathbf{a}| = 515$ nm) of close-packed voids of diameter $d = 500$ nm buried just beneath a planar gold surface. The distance from the planar metal surface to the top of the voids, h, is chosen to be 5 nm, which is much less than the skin depth (25 nm for gold), in order to model a strong coupling of incoming light to the nanoporous metal surface. We also assume that there is a residual dielectric material inside the nanopores, which we account for by a non-unity effective dielectric constant ($\varepsilon_{void} = 1.3$) inside the nanopores [19].

The reflectivity spectra exhibit dips that are associated with excitation of Mie plasmons in the voids, as well as surface plasmon-polaritons (see Fig. 3). The stronger and almost dispersion-less resonances are associated with excitation of Mie plasmons in the voids [7]. The frequencies of these Mie-plasmon resonances are close to the frequencies of the Mie-plasmon modes with orbital quantum numbers $l = 1$ and $l = 2$ of a single void in bulk gold given by Eq. (3) (marked by horizontal lines in Fig. 3). The other (dispersive) resonance in the reflectivity spectra originates from the excitation of surface plasmon-polariton mode [8, 9] with wavevector $\mathbf{q}_{-1,-1}$ on the planar metal surface. The frequency of this mode is close to that of the corresponding surface plasmon-polariton mode estimated in the 'empty lattice approximation' given by Eq. (2) for $(p,q) = (-1,-1)$ (marked by black lines labelled as $\mathbf{q}_{-1,-1}$ in Fig. 3). This mode exhibits an avoided crossing with the first and the second Mie modes at angles of incidence $\approx 20^\circ$ and $\approx 45^\circ$, respectively [9]. The onset frequencies of the Rayleigh anomaly given by Eq. (1) (white lines labelled as $\mathbf{q}_{-1,-1}$ in Fig. 3) is slightly higher than the frequencies of the respective surface plasmon-polariton mode. One can see in Fig. 3 that the Mie plasmon resonances in the specularly-reflected beam quench abruptly (Rayleigh anomaly occurs) starting with the onset of the diffracted beam with in-plane wavevector $\mathbf{q}_{-1,-1}$. The reason for this is that the diffracted beam takes a certain amount of energy out of the specularly reflected beam.

The Mie plasmon resonances in the calculated specular reflection spectra become stronger near grazing incidence [see Fig. 3(b) for $\theta \sim 70^\circ - 80^\circ$]. This behavior can be explained for the $l = 1$ dipolar mode, where the dipole orientation should follow approximately the incident electric field polarization (p-polarization in our case). Therefore, at normal incidence the dipole is buried beneath the metal surface at a depth roughly equal to a half of the void diameter, whereas increasing the angle of incidence produces rotation of the dipole in such a way that its pole becomes closer to the surface of metal, which in turn leads to stronger coupling of the Mie mode with the incident light. Similar arguments can be applied to explain the $l = 2$ mode behavior. However, such an effect is smeared out in the experimental spectra because the light incident at grazing angles is more sensitive to imperfections of the metal surface that lead to additional scattering and this, in turn, results in increased divergence of the reflected beam (see Fig. 3a).

Figure 4 shows the measured and calculated intensity of the first-order diffracted beam with

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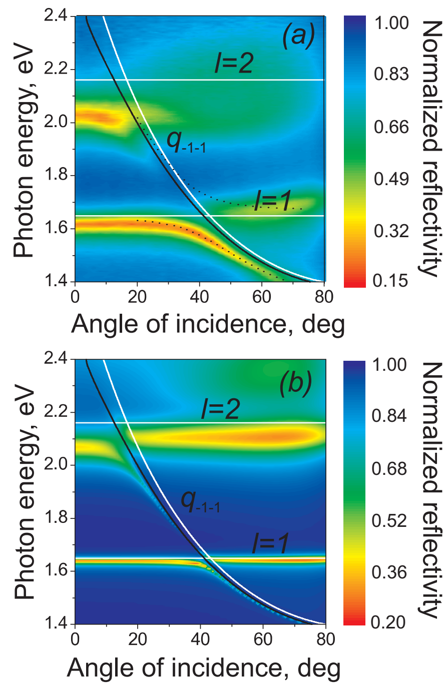

Fig. 3. Specular reflectivity as a function of photon energy $\hbar\omega$ and angle of incidence θ (a) measured from and (b) calculated for a surface of nanoporous gold formed by a hexagonal arrangement of close-packed spherical voids of diameter $d = 500$ nm buried just beneath the metal surface. The plane of incidence is along the $\Gamma - M$ direction (azimuthal angle $\phi = 0$). Black and white lines labeled with q_{-1-1} mark the frequencies of surface plasmon-polaritons and grazing photons, respectively, estimated in the 'empty lattice approximation'. The horizontal white lines mark the energy of the fundamental ($l = 1$) and the second ($l = 2$) Mie-plasmon mode of a single void in bulk gold. The calculated and measured reflectivity spectra are normalized to the reflectivity of a homogeneous planar surface of bulk gold.

in-plane wavevector $\mathbf{q}_{-1,-1}$ as a function of photon energy $\hbar\omega$ and angle of incidence θ. Naturally, the diffracted beam appears only in the frequency/angle-of-incidence region to the right of the dispersion curve for grazing photons with wavevector $\mathbf{q}_{-1,-1}$. However, its intensity becomes strong only at the frequency of the dispersionless resonances associated with excitation of Mie plasmons in the voids. The theoretical results agree qualitatively with experimental data, demonstrating that the diffracted beam takes significant intensity *only* at the Mie plasmon resonances: the intensity of the diffracted beam at Mie plasmon resonance is two orders of magnitude stronger than that off the resonance.

Note that the width of plasmon resonances in the experimental plot is broader than predicted by the theory [cf. Figs. 4(a) and (b)]. One possible reason for such broadening of the plasmon resonances may be the scattering of electrons from the void boundaries [20] in thin membrane-like metal regions between the close-packed voids (not accounted for by the theory here), although the role of additional inhomogeneous plasmon broadening caused by imperfections in the experimental sample (e.g., residual void openings and interconnection of voids) cannot be also ruled out. Our experimental data confirm that the Mie plasmon resonances are much stronger pronounced in samples with thickness, t, approaching the void diameter, d, because the localized Mie plasmon modes are well moulded in almost fully enclosed voids [8].

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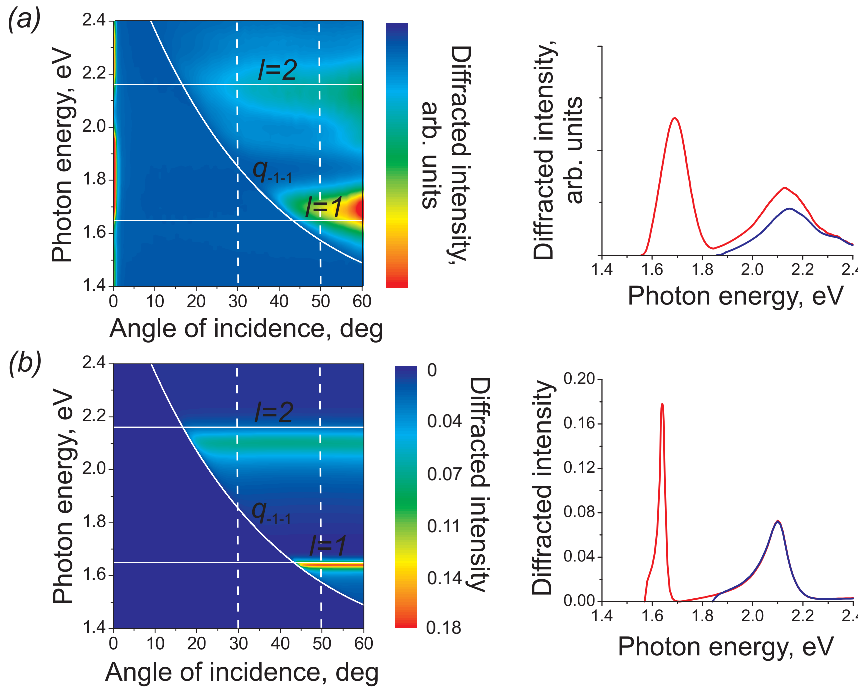

Fig. 4. Intensity of the diffracted beam with in-plane wavevector $\mathbf{q}_{-1,-1}$ as a function of photon energy $\hbar\omega$ and angle of incidence θ (a) measured from and (b) calculated for a surface of nanoporous gold formed by a hexagonal arrangement of close-packed spherical voids of diameter $d = 500$ nm buried just beneath the metal surface. The plane of incidence is along the $\Gamma - M$ direction (azimuthal angle $\phi = 0$). White lines labeled with q_{-1-1} mark the frequencies of grazing photons, estimated in the 'empty lattice approximation'. The horizontal white lines mark the energy of the fundamental ($l = 1$) and the second ($l = 2$) Mie-plasmon mode of a single void in bulk gold. The calculated intensity of the diffracted beam is normalized to the intensity of the incident light. The right panels show the measured and calculated spectra corresponding to two angles of incidence, 30° (blue line) and 50° (red line), marked by dashed white vertical lines in the contour maps.

The frequencies of Mie-plasma resonances can be tuned by varying the diameter of the voids. Figure 5 shows the calculated intensity of the first-order diffracted beam with in-plane wavevector $\mathbf{q}_{-1,-1}$ as a function of photon energy $\hbar\omega$ at a given angle of incidence, $\theta = 50°$, for a surface of nanoporous gold with a hexagonal arrangement of spherical voids of different diameter. Resonances of the diffraction beam intensity follow the blue shift of Mie-plasmon resonances ($l = 1$ and $l = 2$) with decreasing void diameter [7]. The diffracted beam intensity goes down with decreasing void diameter, since fewer electrons (per unit surface area) participate in the void-plasmon mode oscillations.

In the case under consideration the diffracted beam with the in-plane wavevector $\mathbf{q}_{-1,-1}$ preserves the polarization of the incident wave (p-polarization) with respect to the plane of diffraction (which is the plane comprising the wavevector of the diffracted beam and the normal to the metal surface). The plane of diffraction coincides with the plane of incidence, $\Gamma - M$ plane, which is a plane of the mirror symmetry of the structure (see Fig. 2). It can be easily perceived from Fig. 2 that the polar angle of diffraction decreases with increasing the angle of incidence.

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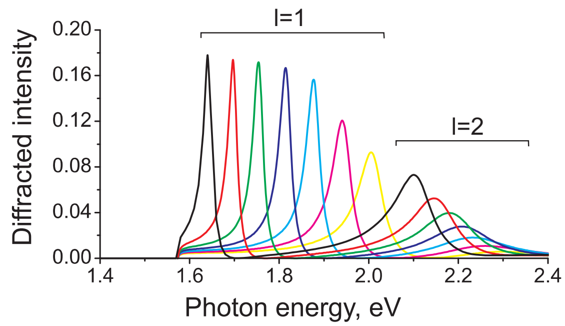

Fig. 5. Calculated intensity of the first-order diffracted beam with in-plane wavevector $\mathbf{q}_{-1,-1}$ versus photon energy $\hbar\omega$ for a surface of nanoporous gold formed by a hexagonal arrangement of spherical voids of different diameter d: from 380 to 500 nm (from right to left, in steps of 20 nm). The angle of incidence is 50°. The lattice constant ($|\mathbf{a}| = 515$ nm) is kept unchanged in these calculations.

In conclusion, the diffracted beam intensity on nanoporous metal surfaces has been shown to be hugely enhanced by excitation of Mie plasmons localized in the voids. Non-dispersive Mie plasmon resonances in voids trigger angle-tolerant frequency-selective excitation of intense diffracted beams in these structures. These effects could be used for characterization of nanoporous metals as well as in the design of various devices for diffraction optics in optoelectronics.

Acknowledgments

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