Surface Shape Resonances in Lamellar Metallic Gratings

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The specular reflectivity of lamellar gratings of gold with grooves 0.5 μm wide separated by a distance of 3.5 μm was measured on the 2000–7000 cm^{-1} spectral range for *p*-polarized light. Experimental evidence of the excitation of electromagnetic surface shape resonances for optical frequencies is given. In these resonances the electric field is highly localized inside the grooves and is almost zero in all other regions. For grooves of depth equal to 0.6 μm, we have analyzed one of these modes whose wavelength (3.3 μm) is much greater than the lateral dimension of the grooves. [S0031-9007(98)06650-2]

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Metallic gratings can exhibit absorption anomalies [1]. One of these anomalies which is particularly remarkable is observed for *p*-polarized light only, and is due to surface plasmon polariton (SPP) excitations. SPP excitation induces a minimum on the specular reflectance spectra which is indicative of the amount of energy flowing parallel to the surface. In a first order approximation, the spectral position of the minimum does not depend on the shape or the amplitude of the grooves, but depends only on the dielectric constant and period of the grating. One interesting problem which was raised a long time ago and which is still of interest today is the near field dependence of these modes on the grating shape [2]. Linked to this problem is the possible existence of modes localized in grooves of prominent shape and their relation with nonlinear optical effects observed in certain rough metal surfaces [3–8].

At the beginning of the century Rayleigh pointed out that flat rigid surfaces with cylindrical holes can present acoustic resonances for well defined depths of the holes [9]. Rayleigh showed that under these resonant conditions the acoustic energy is concentrated in the holes and he suggested that similar effects could occur with light. More recently Rendell and Scalapino [10] suggested the possible existence of localized plasmons in order to explain light emission in metal-oxide-metal structures. These plasmon modes are qualitatively different from propagative SPPs on a flat surface excited by attenuated total reflection or by a gentle surface corrugation. Despite the conceptual and practical interest of these surface shape resonances and well documented theoretical predictions, until now no experimental evidence of these electromagnetic resonances has been reported for optical frequencies.

In this Letter we show that for lamellar gratings with deep rectangular cross sections, localized waveguide resonances which are equivalent to the acoustic resonances described by Rayleigh, can be excited in the channels when the impinging light has an electric field component perpendicular to the grooves direction. The experiments here presented also illustrate the existence of hybrid modes, combination of standing waves localized in the grooves with propagating SPPs.

Measured samples consist in periodic arrays of metallic grooves of nominal width 0.5 μm and separated 3.5 μm. The pattern extends over an area $1 \times 1\ \text{cm}^2$. The samples were prepared on the surface of a silicon wafer by standard photolithography. After development of a negative resist, the sample was etched in SF6 plasma down to the desired depth. The resist mask was subsequently removed by reactive ion etching in an oxygen plasma. Finally, the structured silicon surface was metallized by thermal evaporation of a gold layer. The substrate was rotated during the evaporation in order to coat both the bottom and the walls of the grooves and the average gold layer is about 100 nm thick. Figure 1 shows a scanning electron micrograph of a sample with grooves of depth 0.2 μm. Also in Fig. 1 we show a schematic picture of our samples with a definition of the different parameters: width of the grooves, $a = 0.5\ \mu$m; period of the grating, $d = 3.5\ \mu$m; and angle of incidence of *p*-polarized light, $\theta = 21°$. A Fourier transform spectrometer was used to measure the reflectance of these samples using a flat surface of gold as a reference.

First, computational studies of scattering of plane waves by these lamellar metallic gratings were carried out. Our aim was to analyze the appropriate values for the depths of the grooves that can support surface shape electromagnetic resonances. For that purpose we have used a *transfer matrix* formalism [11] which is ideally suited to work with materials like gold for which the dielectric response disperses with frequency. For these calculations we have used the dielectric functions of gold as tabulated in Ref. [12]. Knowledge of the EM transfer matrix of the system allows us to calculate transmission and reflection coefficients for an incoming plane wave. Once these matrices are obtained the reflectance of the

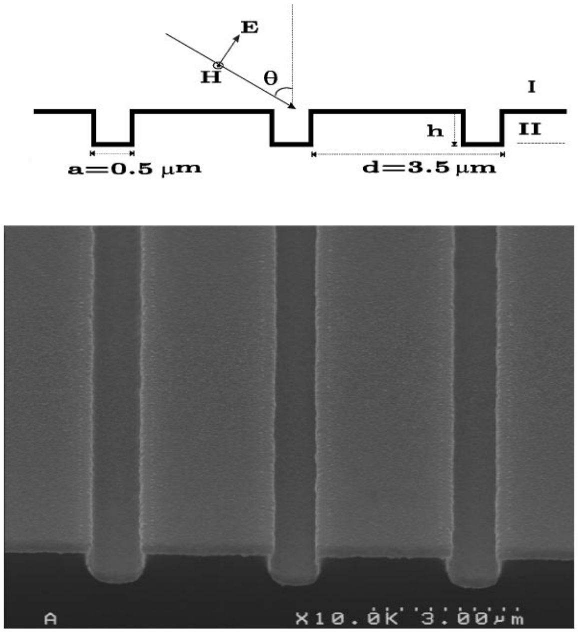

FIG. 1. A scanning electron micrograph of a sample that consists of a metallic grating with grooves of depth $h = 0.2\ \mu$m. In the upper part of this figure we show a schematic view of our samples with grooves of width $a = 0.5\ \mu$m and separated by $d = 3.5\ \mu$m. The incident light is p polarized and the angle of incidence $\theta = 21°$.

grating and a real-space picture of the resulting **E** field can be easily calculated.

Figure 2 displays computed values of the specular reflectance for p-polarized light and angle of incidence $\theta = 21°$ for grooves of different depths as a function of the wave number (k) of the incoming plane wave. We then show how for small values of the depths ($h = 0.1{-}0.2\ \mu$m), the reflectivity minima correspond to SPP excitations as they are observed with an almost flat surface. The energetic positions of these modes are indicated by arrows in Fig. 2. With increasing depth, the resonances are broadened due to radiation damping, and all reflectance minima become inequivalent; the spectral position of some of them ($k = 2100$ and $4450\ \mathrm{cm}^{-1}$) changes only slightly with h, whereas the position of others (in particular the minimum at $k = 4200\ \mathrm{cm}^{-1}$ for $h = 0.1\ \mu$m) depends strongly on the depth of the grooves.

In order to gain physical insight into this problem and explain the different features observed in Fig. 2, we have also carried out an approximated analysis of this scattering process. We take gold as a perfect metal and we assume that, as the wavelength of light is much greater than the width of the grooves, incident light only excites the fundamental eigenmode of the grooves [3]. The amplitude of this excited mode is proportional to $1/D$, the denominator D being

$$D = \cot(kh) - i\,\frac{a}{d} \sum_{n=-\infty}^{\infty} \frac{[\mathrm{sinc}(k\gamma_n a/2)]^2}{(1 - \gamma_n^2)^{1/2}}\,, \qquad (1)$$

with $\mathrm{sinc}(\xi) \equiv \sin\xi/\xi$. $\gamma_n = \sin\theta + \frac{2\pi n}{kd}$ is associated with the nth reflected diffraction order.

The specular reflection coefficient r_0 can be written:

$$r_0 = 1 + 2i\,\frac{a}{d}\,\frac{[\mathrm{sinc}(k\gamma_0 a/2)]^2}{(1 - \gamma_0^2)^{1/2}}\,\frac{1}{D}\,,$$

so the specular reflectance $R_0 = |r_0|^2$ also depends on D.

The zeros in the real part of D are linked to electromagnetic surface resonances; for these particular wave numbers, the amplitude of the fundamental eigenmode of the grooves is maximum provoking a reduction in the specular reflectance [see Eq. (1)]. In Fig. 3 we show the energetic position of the zeros of $\mathrm{Re}(D)$ for $a = 0.5\ \mu$m,

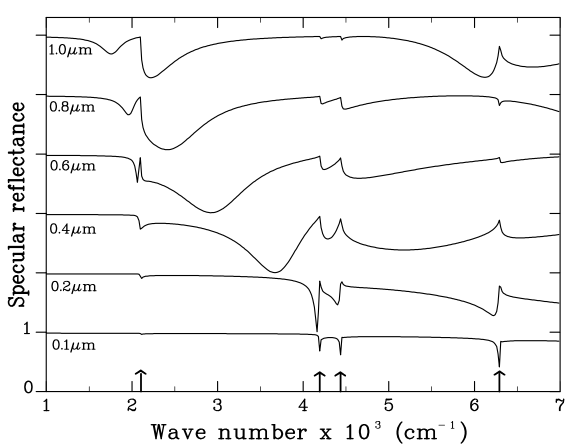

FIG. 2. Calculated specular reflectance of a gold grating with the parameters as defined in Fig. 1. This magnitude is analyzed as a function of the wave number of the incident light for increasing values of the depth of the grooves going from $h = 0.1{-}1.0\ \mu$m. For the sake of clarity each curve is shifted up by +1 with respect to the previous one.

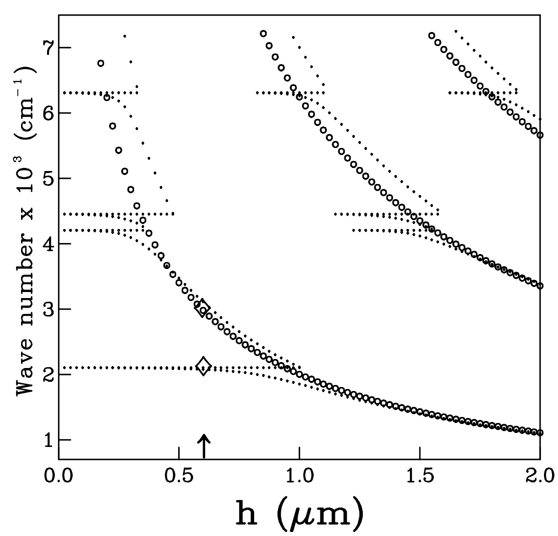

FIG. 3. Energetic positions of zeros of $\mathrm{Re}(D)$ (dots) and waveguide modes localized in the grooves (circles) for different values of the depth of the grooves, h. The locations of the excited modes for $h = 0.6\ \mu$m are marked by diamonds in the figure.

$d = 3.5\ \mu$m, and $\theta = 21°$ as a function of the depth of the grooves (h). For small depths, the electromagnetic resonances are SPPs whose spectral positions can be calculated using a simple diffraction theory. The wave number of these SPPs is given by the diffraction condition $\gamma_n = \pm 1$ [see Eq. (1)] and is located at $k = 2100$ ($n = -1$), $k = 4200$ ($n = -2$), $k = 4450$ ($n = 2$), and $k = 6300$ ($n = -3$) cm^{-1} in the frequency range used in our experiments. For larger depths, however, the excited modes have a hybrid character, combination of SPPs with waveguide modes localized at the grooves. The energetic positions of these waveguide modes for an *isolated* groove of depth h are given by the simple relation $\cos(kh) = 0$. When forming a periodic array, as in our case, the grooves interact electromagnetically and dispersion relations of these waveguide modes change slightly [4] and are displayed by circles in Fig. 3. This figure clearly shows how the spectral locations of excited electromagnetic modes in deep metallic gratings (dots) are the result of hybridization of flat lines associated with SPPs (no dependence with h) and dispersion curves of waveguide modes (circles) that vary with h as $1/h$. For example, the reflectance dip located at 2100 cm^{-1} for $h \to 0$ in Fig. 2 shows no dependence with h for small depths because the hybridization of the SPP mode at this wave number with the corresponding waveguide mode occurs for depths larger than 0.6–0.7 μm. On the contrary, SPP located at 4200 cm^{-1} evolves rapidly with h and for $h = 0.4\ \mu$m its energetic position almost coincides with the position of the corresponding waveguide mode localized in the grooves. This implies that this mode might have a predominant waveguide character. In view of these results, lamellar metallic gratings of period $d = 3.5\ \mu$m with rectangular cross section of width $a = 0.5\ \mu$m and depth larger than 0.4 μm will have at least one surface shape electromagnetic resonance in the optical regime.

In order to observe this surface shape electromagnetic resonance we construct a metallic grating of depth equal to 0.6 μm using the technique described above. For this particular value of h, the surface shape mode is located at around 3000 cm^{-1} and another electromagnetic mode located at 2100 cm^{-1} that in principle should have a predominant SPP character could be observed (see Fig. 3). In Fig. 4 we show the experimental specular reflectance of this sample as a function of the wave number of incoming p-polarized light. Also in this figure we present the corresponding theoretical calculation for this value of h using our *transfer matrix* formalism. Figure 4 shows how incident light is exciting both electromagnetic modes in this metallic grating. The reflectance curve also presents a dip at around 4700 cm^{-1} that, as a difference to the dips located at lower energies, is not associated to a zero of $\mathrm{Re}(D)$ but to a minimum of $|D|^2$. The shape and spectral positions of the different dips are well described by our theoretical model. The experimental features are rounding off due to the angle dispersion of incident beam. The narrow resonance located at 2100 cm^{-1} presents a very high intensity of the **E** field at the upper corners of the grooves (around 300 times larger than intensity of incoming light). Although its energetic location almost coincides with the spectral position of the SPP mode, this resonance already presents a hybrid character and is quite similar to sharp surface plasmon resonances recently observed in deep sinusoidal gratings [13].

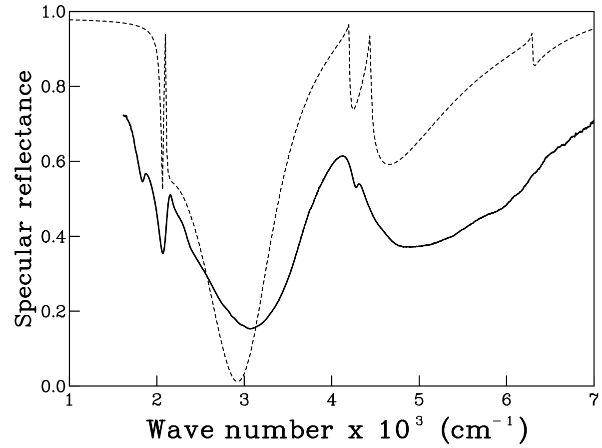

FIG. 4. Experimental (full line) and computed values (dashed line) of the specular reflectance of a gold grating with grooves of depth $h = 0.6\ \mu$m, period $d = 3.5\ \mu$m, and width $a = 0.5\ \mu$m. The angle of incidence is 21°.

Focusing our attention in the surface shape resonance located at around 3000 cm^{-1}, it is interesting to analyze its evolution as a function of the depth of the grooves, h. In other words, how a delocalized SPP at $h \to 0$ evolves to form a localized waveguide mode for larger h. In Fig. 5 we show a detailed picture of the resulting electric fields for different values of h: (a) $h = 0.2\ \mu$m, (b) $h = 0.4\ \mu$m, and (c) $h = 0.6\ \mu$m and wave numbers, k, that correspond to the spectral locations of this surface shape resonance for the values of h analyzed. For $h = 0.2\ \mu$m, the fields are very weak in the grooves and intense at the external surface as it is well known to occur for SPP's modes. With increasing h ($h = 0.4\ \mu$m), the electric field is entering in the grooves and the mode has a clear hybrid character. For $h = 0.6\ \mu$m (the depth of the grooves in our sample), the intensity of the **E** field is mainly concentrated in the grooves and is practically zero in all other regions (vacuum or metal). The maximum intensity in the grooves is around 100 times larger than the intensity of the incoming **E** field and hence at this frequency an enhanced infrared absorption selective to molecules chemisorbed in the grooves is expected. It is interesting to point out that the strength of the **E** field associated with these surface shape resonances is inversely proportional to the ratio between the width of the grooves (a) and period of the grating (d) [see Eq. (2)]. Hence for channels of nanometric dimensions (that could be made today with edge technology) extremely high

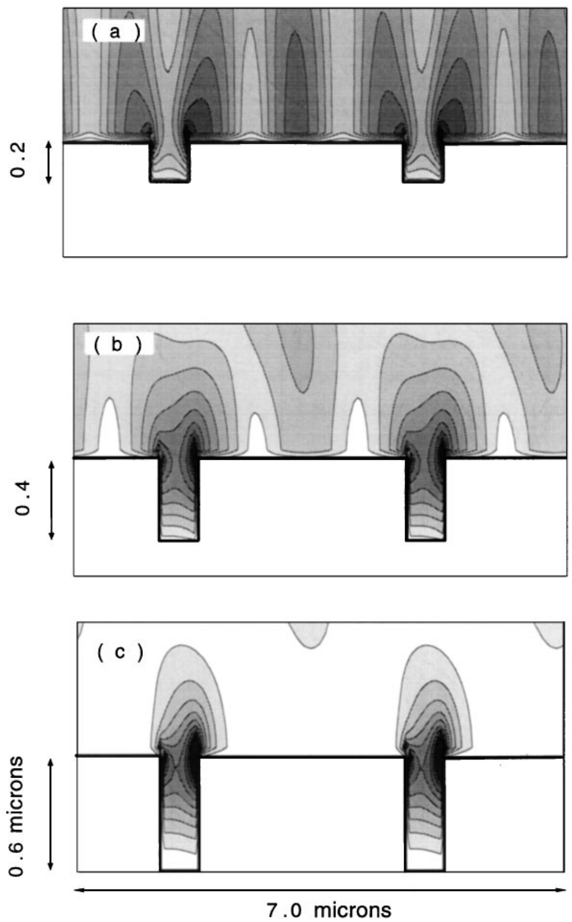

FIG. 5. Detailed pictures of the intensity of the E fields in two unit cells of gold gratings with grooves 0.5 μm wide and 3.5 μm separated. The shape of the grating is also drawn in the figure. The intensities are shown in a gray scale (white: minimum intensity, black: maximum intensity) for different values of h and wave number of incident light: (a) $h = 0.2$ μm ($k = 4160$ cm^{-1}), (b) $h = 0.4$ μm ($k = 3680$ cm^{-1}), and (c) $h = 0.6$ μm ($k = 2920$ cm^{-1}). This last case corresponds to the excitation of a surface shape resonance.

fields can be achieved if the depth of the grooves is properly chosen. However, narrow channels naturally exit at the grain boundaries of poorly crystallized metallic films. Almost a century ago Wood [14] observed optical absorption anomalies of coldly deposited alkali metals which was then attributed to light being trapped in the cavities existing in the metals. Our results suggest that cold deposited films could be particular systems where metallic cavities can support these localized surface shape resonances.

In conclusion, we have observed surface shape resonances for optical frequencies in lamellar metallic gratings with deep rectangular grooves of micron dimensions. For grooves of depth 0.6 μm, we have analyzed one of these resonances located at around 3000 cm^{-1} in which the intensity of the **E** field is highly localized inside the channels. These modes are to some extent similar to the surface plasmons which induce some kind of transparency of the metallic plates with holes of lateral dimension much smaller than the wavelength [15]. The effects here described could also be at the origin of unusual enhancements of infrared absorption of molecules on transparent metallic films [16]. The experiments presented above suggest that composite media including metallic regions in close vicinity could give rise to extremely strong electromagnetic resonances.

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