Why Metallic Surfaces with Grooves a Few Nanometers Deep and Wide May Strongly Absorb Visible Light

J. Le Perchec, P. Quémerais, A. Barbara, and T. López-Ríos

Institut Néel, CNRS and Université Joseph Fourier, BP 166, 38042 Grenoble Cedex 9, France
(Received 15 June 2007; revised manuscript received 31 December 2007; published 15 February 2008)

It is theoretically shown that nanometric silver lamellar gratings present very strong visible light absorption inside the grooves, leading to electric field enhancement of several orders of magnitude. It is due to the excitation of quasistatic surface plasmon polaritons with particular small penetration depth in the metal. This may explain the abnormal optical absorption observed a long time ago on almost flat Ag films. Surface enhanced Raman scattering in rough metallic films could also be due to the excitation of such quasistatic plasmon polaritons in grain boundaries or notches of the films.

DOI: 10.1103/PhysRevLett.100.066408 PACS numbers: 71.36.+c, 42.25.Fx, 42.79.Ag, 73.20.Mf

In general, modifications of metallic surfaces at nanometer scales lead to negligible changes in the reflectivity of the visible and infrared light. However, when the impinging light is combined to surface electromagnetic modes to give rise to surface plasmon polaritons (SPPs), the optical response becomes very surface sensitive. SPPs arouse a lot of interest, as they could play a key role in the issue of merging optics to electronics [1]. The case of long wave vectors has been recently investigated for electromagnetic plane wave guides with nanometer dimensions [2–6] or for the microwave regime [7]. The physics of these highly subwavelength guides is that of coupled SSPs taking birth at the two dielectric-metal interfaces of a metal-insulator-metal system. This coupling splits the SPP dispersion curve into a symmetric and an antisymmetric branch [8,9]. For subwavelength thicknesses of the insulator, the unique guided mode is built by the antisymmetric branch whose dispersion shifts towards the long wave vector as the thickness decreases. In a different context, SPPs were also considered in an attempt to understand the surface enhanced Raman scattering (SERS), and it is currently admitted they are involved in its basic mechanism. SPPs should also be related to a much older misunderstood phenomenon: the abnormal optical absorption (AOA) of alkali metals deposited on a cold glass wall which present absorption bands independently of the incidence angle which cannot be attributed to diffraction or any other known effect [10]. More recently, this abnormal absorption was observed for other metals [11]. Silver films presenting AOA and SERS made by vapor quenching on cold substrates show a typical roughness of shape of 5–30 nm when observed *in situ* with an STM [12]. This is one of the numerous indications that SERS may occur for molecules adsorbed on surfaces presenting a very small amplitude roughness [13]. Up to now, these observations remained partly mysterious because of the nanometer size of the geometrical shapes involved in these phenomena [13]. The absorption of light by SPPs propagating on a flat metallic surface, using a prism, has been known for a long time [14]. Later, following the work of Hessel and Oliner [15], Wirgin *et al.* [16] showed that cavity (Fabry-Perot-like) modes excited inside grooves made on a metallic surface may also participate to the visible light absorption. This was confirmed by next studies [17–21]. However, in all these works, either the grooves' depth h was about 100–400 nm, and roughly related to the exciting light wavelength by $h \sim \lambda/4$, which is the usual Fabry-Perot resonance condition [16] for these kinds of cavities, or the excitation of SPPs propagating on the upper horizontal surface of the gratings was considered.

In the present Letter, we show for the first time that cavities only a few nanometers deep (~5–15 nm) and wide (~2–5 nm), i.e., with depth one order smaller than those considered in all previous studies, may also act as guides and resonators leading to a very strong absorption of visible light ($\lambda \sim 500$ nm). We also show that it is due to the excitation of SPPs in the electrostatic (quasistatic) regime. Our results were obtained by the exact modal method, originally developed by Botten *et al.* [22] and Sheng *et al.* [23], for the grating depicted in Fig. 1, submitted to a p-polarized wave (electric field perpendicular to the grooves). Space is divided into three regions: above ($y > 0$) and below ($y < -h$) the grating (regions I and III, respectively) wherein the magnetic field H_z is expressed as a Rayleigh plane wave expansion, and region II of the grating ($-h < y < 0$) wherein H_z is expressed by a modal expansion. The electric field is obtained from H_z by means of Maxwell's equations. With $\epsilon_{\rm air} = 1$ for sake of simplicity and $\epsilon_{\rm metal} = \epsilon$, the fields are given by [23]

$$H_z^{\rm I}(x,y) = e^{ik(\gamma_0 x - \eta_0^I y)} + \sum_{n=-\infty}^{+\infty} R_n e^{ik(\gamma_n x + \eta_n^I y)}$$

$$H_z^{\rm III}(x,y) = \sum_{n=-\infty}^{+\infty} T_n e^{ik[\gamma_n x - \eta_n^{III}(y+h)]}$$

$$H_z^{\rm II}(x,y) = \sum_{\ell=0}^{+\infty} X_\ell(x)(A_\ell e^{i\Lambda_\ell y} + B_\ell e^{-i\Lambda_\ell y}),$$

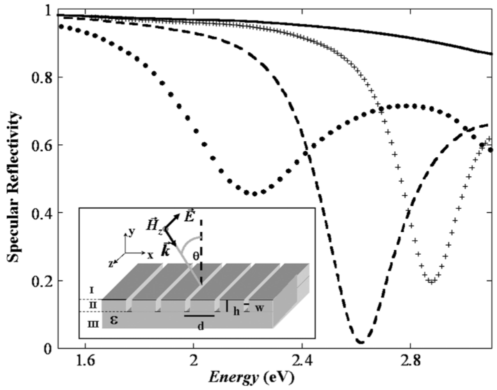

FIG. 1. Reflectivity of a p-polarized plane wave impinging on the silver grating, schematically represented in the insert, at normal incidence calculated with an exact model for different heights $h = 30$ nm (black dot), $h = 15$ nm (dashed line), and $h = 5$ nm (+) with $w = 5$ nm and $d = 30$ nm. The black curve corresponds to the reflectivity of a flat silver film.

where $\gamma_n = \sin\theta + n\lambda/d$, $\eta_n^{\mathrm{I}} = \sqrt{1-\gamma_n^2}$, and $\eta_n^{\mathrm{III}} = \sqrt{\epsilon - \gamma_n^2}$. It is worth noting that the use of the macroscopic dielectric constant of the metal in the calculations is justified since the nanometric spaces concern the air while the metallic part is essentially bulk. H_z^{II} is a linear combination of the eigenmodes $\{X_\ell\}$, each of them being characterized by its eigenwave vector $k_y = \Lambda_\ell$. These are solutions of the eigenvalue equation [22,23]:

$$\cos(kd\sin\theta) = \cos[\beta_\ell(d-w)]\cos(\alpha_\ell w) - \frac{1}{2}\left[\frac{\alpha_\ell \epsilon}{\beta_\ell} + \frac{\beta_\ell}{\alpha_\ell \epsilon}\right]\sin[\beta_\ell(d-w)]\sin(\alpha_\ell w) \qquad (1)$$

where $\alpha_\ell^2 = k^2 - \Lambda_\ell^2$, and $\beta_\ell^2 = k^2\epsilon - \Lambda_\ell^2$, and θ is the incidence angle. Once the fields are expressed in the three regions, we employ the boundary conditions at the horizontal interfaces and project each resulting equation on two different bases [24]. That allows to determine unambiguously the coefficients $\{A_\ell\}$, $\{B_\ell\}$, $\{R_n\}$, and $\{T_n\}$, for $\ell \in [0, L]$ and $n \in [-N, +N]$. Convergency of the solution has been checked by increasing L and N. Typically, $N \sim 400$ and only few modes $L \sim 30$ are enough for all considered cases. For very small w, only the fundamental mode $\ell = 0$ plays a significant role whereas all the others $\ell > 0$ are strongly evanescent in the grooves. We have tested the method by comparing our numerical results with those obtained by two other accurate numerical methods (*RCWA* and *FDTD*) for metallic gratings [19,25]. Figure 1 shows the calculated reflectivity at normal incidence of a silver grating with $d = 30$ nm, $w = 5$ nm, and $h = 30$, 15, and 5 nm. In all cases, we choose $d \ll \lambda$ such that SPPs at the horizontal interface $y = 0$ are never excited in the range of the considered frequencies. The figure shows that a noticeable amount of photons can be absorbed by this very small amplitude grating at specific wavelength in the visible spectrum. It is to note that for $h = 15$ nm, the reflectivity is almost zero at ~2.6 eV (480 nm) whereas that of the flat silver plane stays close to 1. This is a reliable quantitative result for AOA. Figure 2 illustrates that the absorption is due to resonances within the tiny Ag grooves. Indeed, the reflectivity falls are associated with enhancements of the magnetic and electric fields intensity inside the grooves. Enhancements of more than 2 orders of magnitude are achieved for the electric field while the magnetic field is only enhanced by a factor 10–20. The spatial distribution of the normalized magnetic field modulus is represented in Fig. 2(c) considering the grating with $h = 15$ nm and at the resonant energy $\omega = 2.6$ eV. One sees that the subwavelength cavities resonate and absorb most of the photons.

In order to understand why such strong resonances may occur for these shallow grooves, let us return to the SPP dispersion of a flat metal-vacuum interface. For simplicity, we take the dielectric constant of the metal negative and real ($-\infty < \epsilon < -1$). The dispersion is given by the implicit well-known relation $k_\parallel = k\sqrt{\epsilon/(\epsilon+1)}$, where $k_\parallel$ is the SPP wave vector parallel to the interface. As it is known [8], we distinguish two asymptotic regimes: the "optical regime" when $\epsilon \to -\infty$, and the "electrostatic" one when $\epsilon \to -1$. In the optical regime, retardation effects play a significant role [8]. The electromagnetic fields at the interface satisfy $|E_\perp/H| = k_\parallel \approx \omega/c$, and the excited plasmon has a structure very similar to that of light. On the opposite electrostatic regime, retardation effects remain negligible [8]. We have $|E_\perp/H| \to \infty$ and the obtained plasmons have essentially an electric component. In this context, a relevant physical quantity to introduce is the dimensionless ratio $X = \delta_p/\delta_s$, where δ_p is the penetration depth of the SPP in the metal, and δ_s is the usual skin depth in the metal of a plane wave whose wave number is k: $\delta_s^2 = 1/|\epsilon|k^2$ while $\delta_p^2 = -1/k_\perp^2$. For a flat interface, $X = \sqrt{(\epsilon+1)/\epsilon}$. The parameter X satisfies $0 < X < 1$ and completely determines the two regimes: in the optical regime, $X \to 1$ and

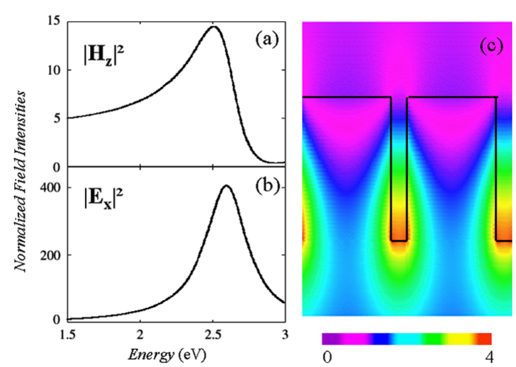

FIG. 2 (color online). Normalized intensities with respect to the incident field of the magnetic field at $y = -h$ (a) and of the electric field along the x-axis at the mouth of the cavity (b), calculated for the grating $h = 15$ nm, $w = 5$ nm, and $d = 30$ nm. (c) Map of the normalized magnetic field modulus near the grating, at the resonance ($\omega = 2.6$ eV).

$\delta_p \approx \delta_s$ while in the electrostatic regime, $X \to 0$ and $\delta_p \ll \delta_s$.

Returning to our grooves with small w, we show that the role played by the decrease of w down to the nanometer scale is to displace the dispersion of the mode guided in the cavities, from the optical regime to the electrostatic one, for a given frequency and thus for a *fixed* ϵ value (Fig. 3). Let us consider the dispersion relation Eq. (1) of the grating in the case of silver and in a range of wave numbers k for which values of ϵ are typically in the interval $-25 < \epsilon < -5$ (visible range). Here again, we neglect the imaginary part of ϵ; we will come back to this approximation later. In the case of subwavelength values of w, it is easy to show that $\Lambda^2_{\ell>0} < 0$ and that the only guided wave in the groove is the fundamental mode whose wave vector is $\Lambda_0^2 > 0$. This mode may satisfy a Fabry-Perot resonance condition when $\Lambda_0 h \sim \pi/2$, as for gratings with deep grooves [16,19], leading to the cavity resonance we are discussing. The problem is to determine the value of Λ_0 and its dispersion. For large enough d and at normal incidence, Eq. (1) may be simplified and factorized so that the fundamental mode fulfills

$$\tan\left(\frac{\alpha_0 w}{2}\right) + \frac{i\beta_0}{\epsilon\alpha_0} \approx 0,$$

where $\alpha_0^2 = k^2 - \Lambda_0^2$, $\beta_0^2 = \epsilon k^2 - \Lambda_0^2$. For small values of $|\alpha_0| w$ (which is always verified for subwavelength w), we get a simple second degree equation for β_0: $\beta_0^2 + (2i/\epsilon w)\beta_0 - (\epsilon - 1)k^2 \approx 0$. We now introduce the same quantity X as for the perfectly flat plane: $X = \delta_p/\delta_s = 1/|\beta_0|\delta_s$. Solving the previous second degree equation in X, we obtain

$$X = \frac{\delta_p}{\delta_s} = \sqrt{\frac{\epsilon}{\epsilon - 1}} f(\Gamma), \qquad (2)$$

where $f(\Gamma) = -\Gamma + \sqrt{\Gamma^2 + 1}$ and $\Gamma = \delta_s/\sqrt{\epsilon(\epsilon - 1)}w$. Notice that Eq. (2) is an almost exact result which is valid whatever k and ϵ are, provided that the imaginary part of ϵ remains small with respect to its real part, and that $w < \lambda$. The function $f(\Gamma)$ satisfies $0 < f(\Gamma) < 1$ and fully characterizes the behavior of the system. The dimensionless parameter Γ reflects the strength of the coupling between the SPPs propagating on the two vertical walls of the grooves. For $\Gamma \ll 1$, the coupling is weak, whereas at strong coupling, $\Gamma \gg 1$. Figure 3 depicts the behavior of X as function of w for silver at $1/\lambda = 20000\ \mathrm{cm}^{-1}$ ($\omega = 2.48$ eV, $\epsilon = -8.57$). By increasing the coupling of the SPPs via the reduction of the widths of the cavities, we can fully scan the different behavior of the usual SPP, from the electrostatic regime to the optical one, with a crossover located around $w = 10$ nm, and that at a given frequency. This allows to have control of the absorption properties of the grating by a simple choice of geometrical parameters. Figure 4 depicts the fundamental mode dispersion, analytically given by

$$\Lambda_0 = \sqrt{\epsilon k^2 - \beta_0^2} = \frac{1}{\delta_s}\sqrt{\frac{1}{X^2} - 1}, \qquad (3)$$

as well as the dispersion obtained by numerical calculation, for two different values of w ($w = 5$ and $w = 30$ nm), and for $d = 300$ nm. The agreement between the numerical and analytical curves is excellent and shows that as w decreases, the wave vector of the guided mode Λ_0 increases even though it is excited by the same incident energy. Meanwhile, we know (Fig. 3) that its penetration depth becomes much smaller than the ordinary skin depth ($X \ll 1$). The dispersion relation of the modes in the optical regime [17,19,26] can be deduced from Eq. (3) taking $\Gamma \ll 1$. Reversely, in the electrostatic regime, $\Gamma \gg 1$, $f(\Gamma) \approx 1/2\Gamma$, and Eq. (3) leads to

$$\Lambda_0 \approx \frac{2}{|\epsilon| w}, \qquad (4)$$

which implies that Fabry-Perot resonances occur for very small values of h, correspondingly to those obtained numerically on Figs. 1 and 2. The electromagnetic field in the groove is dominated by the electric field, $|E_x/H| \gg k$. It is also interesting to notice that since Λ_0 essentially depends on w, we may obtain a scaling law using the condition resonance $\Lambda_0 h \sim \pi/2$. All grooves with nearly the same ratio h/w will resonate around the same frequency. This is

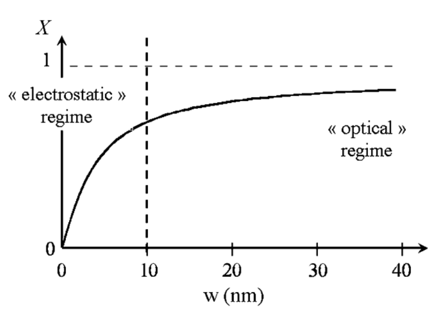

FIG. 3. Evolution of the dimensionless parameter $X = \delta_p/\delta_s$ as a function of the width w of the grooves calculated for $\omega = 2.48$ eV. Modifying w allows to move continuously from one regime to the other, at a *given* frequency.

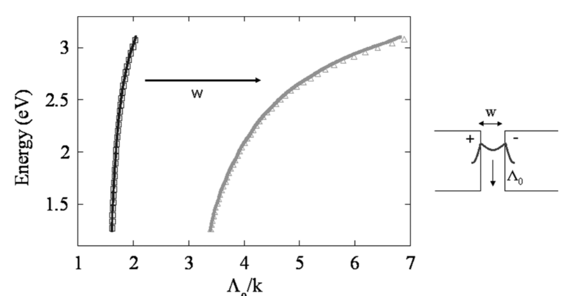

FIG. 4. Dispersion curve of the fundamental guided mode in the grooves calculated for a period $d = 300$ nm and two different widths: $w = 30$ nm (black curve) and $w = 5$ nm (gray curve). Dots correspond to the analytical calculation, and lines correspond to the exact numerical one.

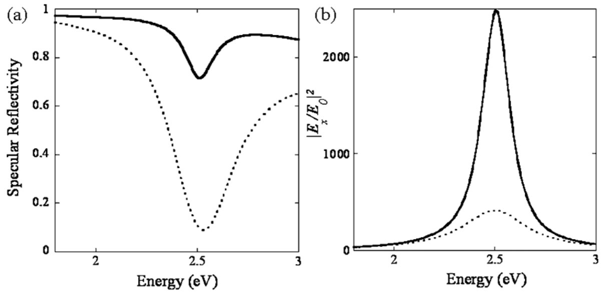

FIG. 5. (a) Reflectivity at normal incidence of two different gratings with nearly the same h/w ratio. $h = 18$ nm and $w = 5$ nm (dashed line) and $h = 3$ nm and $w = 1$ nm (full line) both resonating at the same frequency. (b) Normalized intensity of the electric field along the x-axis at the mouth of the cavities for the two same gratings. Smaller cavities localize much stronger fields (imaginary part of ϵ is taken into account).

shown on Fig. 5, for a grating with $h = 18$ nm and $w = 5$ nm and one with $h = 3$ nm and $w = 1$ nm.

An analytical study of the fields expression shows that $|E_x/E_{\mathrm{inc.}}| \sim 2d/w$, where $E_{\mathrm{inc.}}$ is the amplitude of the total incident field. Considerable electric field enhancements can thus be obtained inside the grooves with small w. Actually, the electrostatic regime is easily obtained provided that the cavities are weakly coupled through the metal; i.e., the grooves are sufficiently distant ($\delta_s < d < \lambda$); otherwise, Λ_0 stays around k. Giant enhancements, obtained for large d/w, are numerically observed: for instance, it is much greater than 10^4 for $w = 1$ nm, $h = 8$ nm, and $d = 200$ nm at $\omega = 1.85$ eV ($\lambda \sim 670$ nm). Finally, it should be observed that turning on a small imaginary part of $\epsilon = \epsilon' + i\epsilon''$, with $\epsilon'' \ll |\epsilon'|$, the resonant wave vector Λ_0 also has an imaginary part Λ_0''. We can show analytically that for $\Gamma \gg 1$: $\Lambda_0''/k''_{\mathrm{plane}} \sim 4/kw$, where $k''_{\mathrm{plane}} = k\epsilon''/(\epsilon')^2$ is the imaginary part of the SPP wave vector of a perfectly flat surface. The attenuation of the SPPs along the walls of the cavity is thus more important than in the case of a single plane surface, for a given frequency. Nevertheless the depth of our channels is as small as the wave vector is long to excite the Fabry-Perot like resonance at $\Lambda_0 h \sim \pi/2$. These modes thus remain slightly attenuated over the length of the channel.

In conclusion, we have shown that the interaction of SPPs between the walls of the grooves drives the change of physical regime from the optical to the electrostatic regime, at a given frequency, i.e., at fixed ϵ. The crossover is around $w = 10$ nm, below which we enter in the electrostatic regime. Consequently, cavity modes which were previously believed to only exist in deep grooves occur for depths which may be up to 100 times shorter than λ. Moreover, the field enhancement concerns essentially the electric part (in the electrostatic regime the wave is not lightlike anymore), which may become a thousand times larger than the one of the impinging light. All this tremendous amount of energy is concentrated *inside* the grooves. Eventually, our calculations suggest that AOA observed on rather smooth metal films may be due to notches of few nanometers deep only, and that SERS could also be due to the excitation of quasistatic surface polaritons in the grooves (giving rise to the so-called "hot spots"), with penetration depths much smaller than the usual skin depth.

The authors wish to thank A. Wirgin, Ph. Lalanne, and S. Collin for useful discussions.

[1] E. Ozbay, Science **311**, 189 (2006).
[2] K. Tanaka and M. Tanaka, Appl. Phys. Lett. **82**, 1158 (2003).
[3] D. F. P. Pile, T. Ogawa, D. K. Gramotnev, T. Okamoto, M. Haraguchi, and M. Fukui, Appl. Phys. Lett. **87**, 061106 (2005).
[4] H. T. Miyazaki and Y. Kurokawa, Phys. Rev. Lett. **96**, 097401 (2006).
[5] S. A. Maier, Opt. Express **14**, 1957 (2006).
[6] Y. Kurokawa and H. T. Miyazaki, Phys. Rev. B **75**, 035411 (2007).
[7] J. R. Suckling, A. P. Hibbins, M. J. Lockyear, T. W. Preist, and J. R. Sambles, Phys. Rev. Lett. **92**, 147401 (2004).
[8] E. N. Economou, Phys. Rev. **182**, 539 (1969).
[9] B. Prade, J. Y. Vinet, and A. Mysyrowicz, Phys. Rev. B **44**, 13556 (1991).
[10] R. Wood, Phil. Mag. **38**, 98 (1919).
[11] O. Hunderi and H. P. Myers, J. Phys. F **3**, 683 (1973); H. P. Myers, *ibid.***3**, 1078 (1973); **6**, 141 (1976).
[12] C. Douketis, Z. Wang, T. L. Haslett, and M. Moskovits, Phys. Rev. B **51**, 11022 (1995).
[13] M. Moskovits, Rev. Mod. Phys. **57**, 783 (1985).
[14] A. Otto, Z. Phys. **216**, 398 (1968).
[15] A. Hessel and A. A. Oliner, Appl. Opt. **4**, 1275 (1965).
[16] A. Wirgin and T. López-Ríos, Opt. Commun. **48**, 416 (1984); **49**, 455 (1984).
[17] M. B. Sobnack, W. C. Tan, N. P. Wanstall, T. W. Preist, and J. R. Sambles, Phys. Rev. Lett., **80**, 5667 (1998).
[18] W. C. Tan, T. W. Preist, J. R. Sambles, and N. P. Wanstall, Phys. Rev. B, **59**, 12661 (1999).
[19] S. Astilean, P. Lalanne, and M. Palamaru, Opt. Commun. **175**, 265 (2000).
[20] I. R. Hooper and J. R. Sambles, Phys. Rev. B, **66**, 205408 (2002).
[21] E. Popov, N. Bonod, and S. Enoch, Opt. Express **15**, 4224 (2007).
[22] L. C. Botten, M. S. Craig, R. C. McPhedran, J. L. Adams, and J. R. Andrewartha, J. Mod. Opt. **28**, 1087 (1981); **28**, 1103 (1981).
[23] P. Sheng, R. S. Stepleman, and P. N. Sanda, Phys. Rev. B **26**, 2907 (1982).
[24] J. Le Perchec, Ph.D. dissertation, Grenoble, 2007 (unpublished).
[25] F. I. Baida and D. Van Labeke, Phys. Rev. B **67**, 155314 (2003).
[26] S. Collin, F. Pardo, and J. L. Pelouard, Opt. Express **15**, 4310 (2007).