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Light emission from surface-plasmon and waveguide modes excited by N atoms near a silver grating

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We examine the coupling of excited N atoms, at distances d away from a silver grating, to the usually nonradiative surface-plasmon and waveguide modes of a metal-dielectric-vacuum system. For $d<(\epsilon_D-1)^{-1/2}\lambda/4$, where ϵ_D is the dielectric constant of the dielectric layer and λ is the wavelength of light at the frequency of the excitation, only the surface-plasmon mode exists. It is directly excited by the near field of the N atoms and radiates via the grating. For $d\geq(\epsilon_D-1)^{-1/2}\lambda/4$, waveguide modes also exist. They also can decay radiatively via the grating. Conservation of momentum parallel to the surface to within an integer number of Bloch waves of the grating determines the angular distribution of the emitted radiation. The agreement between the experimentally measured and theoretically predicted angular distributions is excellent. The dielectric constant of condensed N_2 is deduced to be $\epsilon_D=1.51\pm0.02$ at $\lambda=523$ nm.

I. INTRODUCTION

A metal surace in contact with a dielectric of thickness d can support both surface-plasmon and waveguide modes if the thickness d is on the order of the wavelength of light or greater.[1-4] If d is less than $(\epsilon_D-1)^{-1/2}\lambda/4$, only the surface-plasmon mode may propagate.

Both surface-plasmon and waveguide modes travel parallel to the metal-dielectric interface and are nonradiative for smooth surfaces. If, however, the interface is rough, then the modes may radiate.[1,4,5] If the form of the roughness is a periodic grating, then the momentum conservation requirement parallel to the interface may be relaxed by $\pm$ an integer number of Bloch waves of the grating (i.e., an integer times $2\pi\lambda/L$ where L is the grating periodicity).[1-3,5-7] Thus, these modes become radiative at specific angles. One mode may be radiative at more then one angle, corresponding to more than one integer.

We report the coupling of excited nitrogen atoms, at distances d away from a silver grating, to both surface-plasmon and waveguide modes. Other workers have previously reported on the coupling of electronically excited dipoles to surface plasmons on smooth[8-13] and rough[13-17] surfaces. Only Lukosz and Meier[18,19] have studied the distance dependence of both surface-plasmon and waveguide modes excited by dipoles near a surface. They used a method similar to attenuated total internal reflection to get the modes to radiate. In our experiments, the grating strongly mediates both the coupling of nitrogen atoms to the waveguide modes and the subsequent reradiation of both waveguide and surface-plasmon modes. [As reported in a previous paper,[14] the dominant method of excitation of the surface-plasmon mode at small d ($d<<\lambda$) is by way of the near field of the nitrogen atoms, rather than radiatively by way of the grating.] Since the grating relaxes the momentum conservation requirement parallel to the surface so that these usually nonradiative modes may now radiate at certain angles, they can be probed by examining the radiation pattern of the coupled vacuum—nitrogen-atom—N_2-dielectric—silver-grating system.

The radiation pattern as a function of d is calculated and compared to the experimental observations with excellent agreement. p (TM) and s (TE) polarized modes are compared, the dielectric constant of nitrogen is deduced to be $\epsilon_d = 1.51 \pm 0.02$ at $\lambda = 523$ nm, and waveguide modes are examined as they "turn on" and "turn off" with increasing d.

II. EXPERIMENTAL

Figure 1 shows the geometry of the experiment. Nitrogen films of thickness d were condensed under ultrahigh-vacuum conditions (residual gas pressure typically 2×10^{-7} Pa) onto a chilled silver grating. The silver grating was produced by evaporating 300 nm of silver onto a holographic photoresist grating on a sapphire substrate. The photoresist grating was made by exposing a spun-on layer of Shipley AZ1350 photoresist to two expanded interfering beams of an Ar^+ laser (wavelength of 457.9 nm). The wavelength L and half-height δ of the grating were $L = 846.5$ nm and $\delta = 40 \pm 20$ nm. L and δ were calculated from the reflectivity and diffraction efficiency of the grating.[20]

The grating was chilled with a closed-cycle He refrigerator to approximately 10 K. The thickness of the nitrogen films condensed onto the grating was determined from exposure (pressure $\times$ time), using a calibration factor 1100 nm/(Pa sec), that was determined previously for this same apparatus.[13,21]

A small spot (1×10^{-5} m^2) on the nitrogen film was excited by 100-eV electrons (0.5 μA, penetration depth ~ 1.7 nm, Ref. 21) for 4 sec to produce a thin layer of N atoms in an excited state at a distance d from the substrate. The phosphorescent intensity of the green N $^2D \rightarrow {}^4S$ transition ($\lambda = 523$ nm, $\tau_0 \approx 40$ sec) was then measured in the following 4 sec as a function of polar angle θ, at constant azimuthal angle $\phi = 90°$. Because of the size of the observation port on the UHV system, observed polar angles were restricted to $4° \leq \theta < 40°$ at the fixed azimuthal angle $\phi = 90°$. The angular resolution of the detector (phototube, interference filter, and polaroid filter) was $\pm 0.8°$. The estimated precision and accuracy of the angular measurements were $\pm 0.1°$ and $\pm 0.4°$, respectively. The polaroid filter was used to analyze the detected light for p (TM radiation) and s (TE radiation) polarized components. Since the electron beam was off while scanning θ, none of the detected light was the result of surface electromagnetic modes directly excited by electrons. (Typical surface electromagnetic mode decay times are $\lesssim 10^{-14}$ sec.[1])

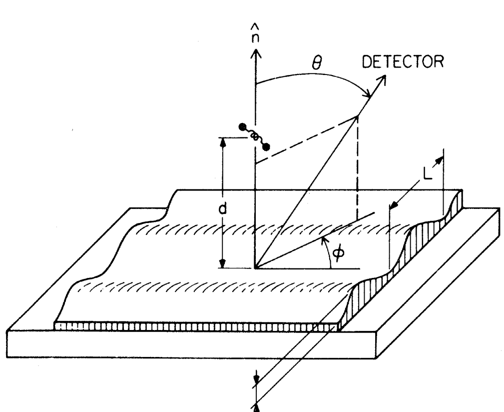

FIG. 1. Geometry of the holographic grating. $L = 846.5$ nm is the grating periodicity, $\delta \approx 40$ nm is the half-height of the grating bumps, and d is the thickness of the condensed N_2 film. The azimuthal angle was $\phi = 90°$ for this experiment. The observation port allowed light emitted at polar angles of $4° \leq \theta \leq 40°$ to be measured.

III. RESULTS AND DISCUSSION

Figure 2 shows the results of s- and p-polarized scans of polar angles $4° \leq \theta \leq 40°$ for a nitrogen film of thickness $d = 2000$ nm. Note that both s- and p-polarized scans show intense peaks at polar angles greater than 22.4° while there are less intense peaks for polar angles less than 15°. No peaks occur between 15° and 22.4°.

The dependence of the peak positions on nitrogen condensate thickness is shown in Fig. 3. The theoretical curves are obtained by calculating the wave vectors of each guided mode that propagates

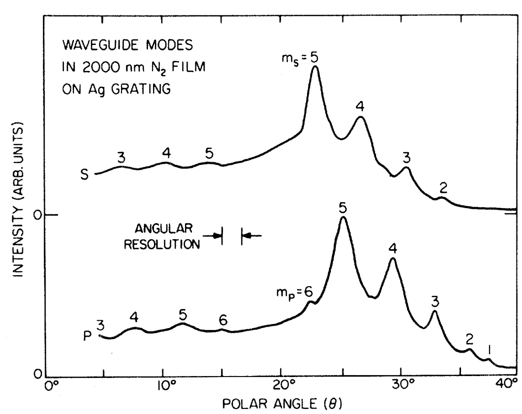

FIG. 2. Intensity of s- and p-polarized light vs polar angle for excited N atoms on a 2000-nm N_2 film on a Ag grating. The numbers refer to the number of nodes in the transverse field between the metal N_2 and N_2 vacuum interfaces. $m_g = 1$ events (one unit Bloch wave of grating momentum) occur at $22.4° \leq \theta \leq 37.5°$. $m_g = 2$ events occur for $\theta < 15°$. $m_g = 3$ events (not shown) should occur at $\theta > 40°$.

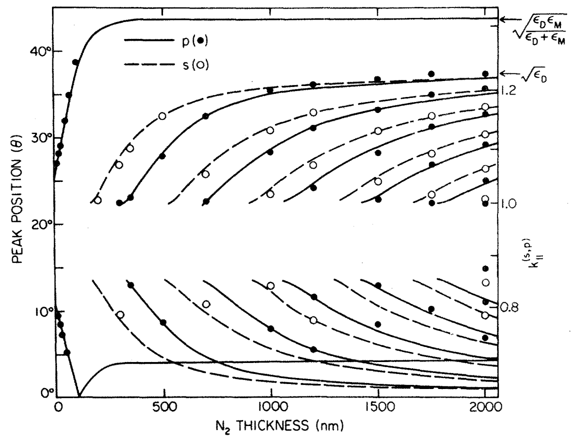

FIG. 3. Angular peak positions at which light is emitted as a function of N_2 thickness d. $m_g=1$ events (one unit Bloch wave of grating momentum) are on the upper half and $m_g=2$ events are on the lower half. The surface plasmon mode begins at $\theta=25.3°$ at $d=0$ ($\sin 25.3°=[\epsilon_M/(1+\epsilon_M)]^{1/2}-\lambda/L$). At $d=\infty$ the surface-plasmon mode goes to $\sin\theta=[\epsilon_D\epsilon_M/(\epsilon_D+\epsilon_M)]^{1/2}-\lambda/L$. The waveguide modes begin at $\sin 22.4°=1-\lambda/L$, while at $d=\infty$, $\sin 37.6°=\epsilon_D^{1/2}-\lambda/L$.

along a silver surface with an N_2 coating of thickness d. The bare metal supports only the p-polarized surface plasmon. The presence of a dielectric coating on the metal surface substantially alters the properties of the surface plasmon, and moreover, allows the surface to guide additional modes of both polarizations.[1-4] Such a configuration can be thought of as a slab waveguide.[22] The spectrum of guided modes is a function of overlayer thickness d and frequency ω, which is determined by the following eigenvalue equations for s (TE) and p (TM) modes:

$$\tan(\tilde{k}_\perp^D d)=\frac{\tilde{k}_\perp^D(\tilde{k}_\perp^V+\tilde{k}_\perp^M)}{(\tilde{k}_\perp^D)^2-\tilde{k}_\perp^V\tilde{k}_\perp^M} \tag{1a}$$

for the s mode ,

$$\tan(\tilde{k}_\perp^D d)=\frac{\tilde{\epsilon}_D\tilde{k}_\perp^D(\tilde{\epsilon}_M\tilde{k}_\perp^V+\tilde{k}_\perp^M)}{\tilde{\epsilon}_M(\tilde{k}_\perp^D)^2-\epsilon_D^2\tilde{k}_\perp^V\tilde{k}_\perp^M}$$

for the p mode , (1b)

where

$$\tilde{k}_\perp^V=[\tilde{k}_{||}^2-(\omega/c)^2]^{1/2} , \tag{2a}$$

$$\tilde{k}_\perp^D=[\epsilon_D(\omega/c)^2-\tilde{k}_{||}^2]^{1/2} , \tag{2b}$$

$$\tilde{k}_\perp^M=[\tilde{k}_{||}^2-\tilde{\epsilon}_M(\omega/c)^2]^{1/2} , \tag{2c}$$

are complex, and ϵ_D and ϵ_M are the frequency-dependent dielectric functions of the coating and metal, respectively.[22] The superscripts V, D, and M refer to vacuum, dielectric, and metal, respectively. Any value of $\tilde{k}_{||}$ with $\mathrm{Re}\,(\tilde{k}_{||})>\omega/c$ which solves either eigenvalue equation corresponds to a guided mode.

Consider a frequency ω less than the surface-plasmon frequency ω_{sp}, and let λ be the free-space wavelength at ω ($\lambda=2\pi c/\omega$). For $d<(\epsilon_D-1)^{-1/2}\lambda/4$ the surface supports only the surface-plasmon guided mode. As d increases, s and p modes appear alternately. The mth order s mode (m_s) appears at

$$d_s=\frac{(2m_s+1)\lambda}{4\sqrt{\epsilon_D-1}} , \tag{3a}$$

whereas the mth order p mode appears at

$$d_p=\frac{m_p\lambda}{2\sqrt{\epsilon_D-1}} . \tag{3b}$$

This behavior is illustrated in Fig. 3 where the guided mode reduced wave vectors, defined as $k_{||}^{(s,p)}=\mathrm{Re}(\tilde{k}_{||}^{(s,p)})c/\omega$, of a N_2 coated Ag surface at $\lambda=523$ nm are plotted as a function of N_2 coating thickness. (See the right-hand ordinate in Fig. 3 for values of $k_{||}^{(s,p)}$.) These dispersion relations are plotted for a flat metal surface using $\epsilon_D=1.50$ and $\epsilon_M=-11.56+i\,1.673$.

Figure 4 shows the x component (longitudinal) of the E and H fields associated with the surface-plasmon and waveguide modes for a few N_2 thicknesses. At first, only the p-polarized surface plasmon can propagate, but as the N_2 thickness increases, s and p waveguide modes alternately come in. For s modes E_y, H_z, and H_x exist, while p modes have H_y, E_z, and E_x fields (x is the direction of propagation, z is the direction perpendicular to the surface). The mth order s or p made has m nodes in its longitudinal (x) field component as a function of z between the two interfaces. At the Ag-N_2 interface the magnitude of E field tends to be larger for p than for s modes.

A periodic grating couples the surface electromagnetic waves to visible light. To determine the angles at which the light will be emitted, we consider momentum conservation parallel to the surface. Using the reduced wave vectors of the surface-plasmon or waveguide modes parallel to the surface $k_{||}^{(s,p)}$, one can write

$$k_{||}^{(s,p)}=k_{||}^{\gamma}+\frac{\lambda}{L}m_g=\epsilon^{1/2}\sin\theta+\frac{\lambda}{L}m_g , \tag{4}$$

where $k_{||}^{\gamma}$ is the reduced photon parallel momen-

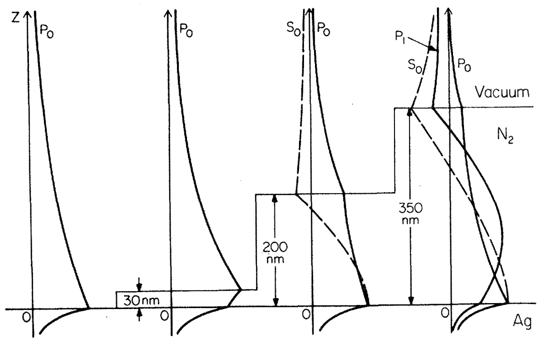

FIG. 4. Schematic representations of E_x (magnitude of the E field parallel to the surface and to the direction of propagation x) for p modes and H_x (magnitude of the H field parallel to the surface) for s modes at several N_2 thicknesses d. The effect of increasing d for $d << \lambda$ is to compress the field of the surface plasmon ($m_p=0$) toward the Ag surface. As more N_2 is added (d increasing) first an s waveguide mode turns on ($m_s=0$ where m_s is the number of nodes in the H field), and then with more N_2 a p waveguide mode with one node turns on ($m_p=1$). More s and p modes turn on alternately with further increase in d.

tum, L is the grating periodicity, m_g is an integer, and ϵ is the effective mode and thickness-dependent dielectric function of the N_2 layer on the Ag.[4] Since $k_{||}^{(s,p)} > \epsilon^{1/2}$, solutions to Eq. (4) require $m_g > 0$. Equation (4) now relates $k_{||}^{(s,p)}$ to the polar angle as plotted in Fig. 3. The peaks at $\theta > 22.4°$ correspond to $m_g=1$ events while the smaller peaks at $\theta < 15°$ correspond to $m_g=2$ events.

The relative intensities of the $m_g=1$ peaks ($\theta > 22°$) in Fig. 2, and peak positions as a function of d in Fig. 3, show how the modes turn on and off. When a waveguide mode first appears at d_p or d_s [see Eq. (3)], it is not intense but rapidly increases in intensity and moves to a slightly larger angle with increasing d. The modes turn on at about 22.4° ($d \approx d_p$ or d_s; see $m_p=6$ in Fig. 2), build to an intensity maximum at about 24° ($d \approx 1.1 d_p$ or 1.1 d_s; see $m_p=5$ or $m_s=5$ in Fig. 2), and then slowly decrease in intensity toward zero with increasing d as they asymptotically approach $\theta_a \approx 37.6°$ (at $d=5d_p$ the position of a p waveguide mode is $\sim 37°$ and near zero intensity; see $m_p=1$ in Fig. 2). This asymptotic value θ_a can be used to measure the dielectric constant of condensed N_2 since $\epsilon_D^{1/2} = \sin\theta_a + \lambda/L$. This gives $\epsilon_D = 1.51 \pm 0.02$. This is the only adjustable parameter that was used in obtaining the fits of Fig. 3.

The s modes were less intense than the p modes and could not be followed to their asymptotic "turn off" point. $m_s=2$ was the lowest order s mode observable for $d=2000$ nm, whereas the p modes corresponding to $m_p=1,2$ were visible even though they occurred at larger angles (had turned on at smaller d).

IV. SUMMARY

By observing the radiation pattern of excited N atoms ($\lambda = 523$ nm) at well-defined distances d from a silver grating of wavelength $L = 846.5$ nm we have found the following.

(1) Both surface-plasmon and waveguide modes can be excited by N atoms. The surface plasmon is efficiently excited by the near-field of the N atom at small d. The waveguide modes only exist at larger d [$d \gtrsim (\epsilon_D - 1)^{-1/2}\lambda/4$].

(2) The excitation of the waveguide modes and the radiative decay of both surface-plasmon and waveguide modes is governed by conservation of momentum parallel to the surface. See Eq. (4). Neither the surface-plasmon nor the waveguide modes are radiative if roughness (i.e., the grating) is not present. Both $m_g=1$ and $m_g=2$ modes of decay are observed, where m_g is the number of unit Bloch waves of the grating.

(3) The distance dependence of both surface-plasmon and waveguide mode peak positions agree well with theory. Both $m_g=1$ surface-plasmon and $m_g=1$ waveguide modes move to larger angles ($k_{||}^{(s,p)}$ increase) with increasing d.

(4) The dielectric constant of a thin film of N_2 condensed on silver is calculated to be $\epsilon_D = 1.51 \pm 0.02$ by fitting the experimentally measured curves, specifically, by fitting the angle that the $m_p=1$ waveguide mode asymptotically approaches at large d.

(5) The waveguide modes are weak at d_p on d_s, the nitrogen thickness at which they first turn on, but quickly reach a maximum in intensity at about $1.1d_p$ or $1.1d_s$ and then slowly decrease in intensity with increasing d.

(6) The p waveguide modes are slightly more intense than the s waveguide modes, possibly due to the larger fields of the p modes at the Ag grating surface and hence better coupling through the Ag grating to the radiative continuum.

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[1] H. Raether, *Excitation of Plasmons and Interband Transitions by Electrons* (Springer, New York, 1980), pp. 112–171.

[2] K. Holst and H. Raether, Opt. Commun. 2, 312 (1970).

[3] I. Pockrand, Opt. Commun. 13, 311 (1975).

[4] Z. Schlesinger and A. J. Sievers, Appl. Phys. Lett. 36, 409 (1980).

[5] D. Heitmann and H. Raether, Surf. Sci. 59, 17 (1976).

[6] J. C. Tsang, J. R. Kirtley, and T. N. Theis, Solid State Commun. 35, 667 (1980).

[7] A. Girlando, W. Knoll, and M. R. Philpott, Solid State Commun. 38, 895 (1982).

[8] R. R. Chance, A. Prock, and R. Silbey, Adv. Chem. Phys. 37, 1 (1978).

[9] K. H. Drexhage, M. Fleck, F. P. Shafer, and W. Sperling, Ber. Bunsenges. Phys. Chem. 20, 1179 (1966).

[10] I. Pockrand, J. D. Swalen, R. Santo, A. Brillante, and M. R. Philpott, J. Chem. Phys. 69, 4001 (1978).

[11] W. Lukosz and R. E. Kunz, Opt. Commun. 31, 42 (1979).

[12] W. H. Weber and C. F. Eagen, Opt. Lett. 4, 236 (1979).

[13] A. Adams, R. W. Rendell, W. P. West, H. P. Broida, P. K. Hansma, and H. Metiu, Phys. Rev. B 21, 5565 (1980).

[14] A. Adams, J. Moreland, and P. K. Hansma, Surf. Sci. 111, 351 (1981).

[15] W. Knoll, M. R. Philpott, J. D. Swalen, and A. Girlando, J. Chem. Phys. 75, 4795 (1981).

[16] C. F. Eagen (unpublished).

[17] P. K. Aravind, E. Hood, and H. Metiu, Surf. Sci. 109, 95 (1981).

[18] W. Lukosz and M. Meier, Opt. Lett. 6, 251 (1981).

[19] W. Lukosz, J. Opt. Soc. Am. 71, 744 (1981).

[20] D. Heitmann, Opt. Commun. 20, 292 (1977).

[21] A. Adams and P. K. Hansma, Phys. Rev. B 22, 4258 (1980).

[22] D. Marcuse, *Theory of Dielectric Optical Waveguides* (Academic, New York, 1974), pp. 7–15.