Photoacoustic study of plasmon resonance absorption in a diffraction grating

T. Inagaki, M. Motosuga, and K. Yamamori
Department of Physics, Osaka Kyoiku University, Tennoji, Osaka 543, Japan

E. T. Arakawa
Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830
(Received 21 March 1983)

Plasmon resonance absorption in a 520-line/mm silver-coated diffraction grating was measured as a function of the angle of ruling orientation relative to the plane of photon incidence by a photoacoustic method. The experimental results of absorptance changes as a function of ruling orientation were found to be consistent with predictions from the first-order perturbation theory for roughness-induced photoabsorption. A discrepancy was found, however, between the absorptance values observed and the values calculated from the first-order theory.

I. INTRODUCTION

In recent years photoacoustic measurements have been used to study photoabsorptions in thin metal films and metal surfaces. This relatively new experimental technique[1] probes absorption of photons by detecting heat production resulting from nonradiative dissipation of excited states created by incident photons. In this respect, the technique may be considered to be analogous to calorimetry[2] which has long been used in the field of optical spectroscopy of metals. We have recently employed[3–5] the photoacoustic technique to observe nonradiative relaxation of surface plasmons in thin silver films and determined the probability of roughness-aided radiative relaxation. In these studies surface plasmons have been excited in thin silver films by the method of attenuated total reflection (ATR). It is well known[6] that direct optical excitation of nonradiative surface plasmons is also possible by the use of diffraction grating coupling. Surface plasmon excitation aided by topological structure has attracted[7–16] a great deal of attention for many years, and, in recent years, its importance in a range of surface phenomena such as surface enhancement of Raman scattering has been emphasized in many studies.[16] The present paper deals with experimental results and interpretation of plasmon resonance absorption in a metal-coated diffraction grating measured by the photoacoustic technique.

Measurements were made of the plasmon resonance absorption as a function of ruling orientation of a diffraction grating with respect to the plane of photon incidence. To our knowledge, no studies of these absorptions have been made previously. Earlier, Teng and Stern[7] observed shifts of plasmon resonance angles when rotating a diffraction grating around the grating normal. The lack of measurements of absorption is due to difficulties associated with conventional optical techniques.

In order to couple incident photons to surface plasmons on the surface of a diffraction grating, it is necessary for the reciprocal grating vector or its multiples to be added to or subtracted from the component of the wave vector of the incident photon parallel to the grating surface. The excited surface plasmons may then decay, in general, into photons by losing or gaining the grating vector or its multiples upon scattering by the grating structure during propagation along the grating surface. The probabilities of these photon-to-plasmon and plasmon-to-photon conversions depend strongly on the groove profile of the diffraction grating. These phenomena are manifested as peaks and dips in diffraction efficiency curves measured as a function of angle of incidence (or wavelength), corresponding to excitation and radiative deexcitation of surface plasmons, respectively, or their combination and have long been known as Wood's anomalies.[17] To determine plasmon resonance absorption quantitatively, it is necessary to measure intensities R_m of each diffracted order m relative to the incident intensity as a function of angle of incidence and sum them to deduce the absorption $A=1-\sum_m R_m$. Such studies have been made previously by Hutley and Bird[11] and by Rothballer,[15] the latter finding that there is an optimal groove depth for which resonance absorption occurs most efficiently. These studies are limited, however, to the case of ruling orientation perpendicular to the plane of photon incident, for which only p-polarized photons may be converted into surface plasmons. If the ruling is not perpendicular to the plane of incidence, both p- and s-polarized photons are converted into surface plasmons. Photons are now diffracted into directions out of the plane of incidence, and the measurement of intensities of each diffracted order as a function of angle of incidence becomes quite difficult. In such a case, the present photoacoustic technique, which measures absorption directly by probing the subsequent heat generation, has an obvious advantage over the conventional optical method used by the previous authors.

An observation which is closely related with the present photoacoustic studies has been reported previously by Hutley and Maystre,[14] who observed a significant temperature rise of a metal-coated holographic grating when the angle of incidence of a laser beam approached the plasmon resonance angle.

II. EXPERIMENT

The diffraction grating used in the present study was a 520-line/mm plastic replica grating coated with a vacuum-evaporated silver film. The groove depth relative to the mean surface was evaluated to be 16 ± 1 nm from measurement of the first-order diffraction intensity for normal incidence by the method described by Pockrand and Raether.[18] The groove profile examined by scanning-electron-microscope (SEM) observation appeared to be nearly symmetric trapezoidal. However, it was difficult to determine exact groove parameters.

The basic design of our photoacoustic cell was the same as one described earlier.[3,4] The cell frame, equipped with a tiny condenser microphone and a glass window, was attached to the diffraction grating surface and sealed with vacuum grease. A 633-nm photon beam from a 1-mW He-Ne laser incident through the glass window was used to excite plasmons in the diffraction grating. The incident beam was chopped at 300 Hz by a mechanical light chopper, and the photoacoustic signal was detected by an ultrasensitive lock-in amplifier (NF Circuit Block, Model LI-574).[3,4]

Interpretation of the experimental results of the photoacoustic (PA) signal was straightforward. The photoacoustic property of the silver film which coated the grating surface was characterized[1,19] by the thermal diffusion length μ_s, optical absorption length μ, and film thickness l. For a chopping frequency of 300 Hz, $\mu_s = 4.27\times10^5$ nm, and μ was evaluated to range from 11.5 to 11.7 nm for different angles of photon incidence by using the literature value[20] of the optical constants of silver. The silver film was vacuum evaporated to a thickness $l \simeq 3.00\times10^2$ nm, and hence it was a thermally thin and optically thick sample, satisfying $\mu_s \gg l \gg \mu$. By using the Rosencwaig and Gersho theory[1,19] for PA signal generation from solids, one may calculate that the PA signal from such a sample is saturated[19,21] and hence is proportional to the optical absorptance $A = 1 - R$, where R is the reflectance. This has been verified experimentally.[22]

In order to determine the absorptance from the PA signal, it was necessary to know the response constant of our photoacoustic cell. For this purpose, simultaneous measurements[3-5] of the PA signal and the reflectance were made with smooth silver films. Since the PA signal from a thermally thin sample depends[1,19] on the thermal properties of the substrate, the response constant had to be determined with a film on the same substrate as of the film on the diffraction grating studied. Photoacoustic measurements were, therefore, performed on the silver film deposited on the unruled portion of the replica grating. Since this silver film exhibited an appreciable amount of diffuse light scattering, reflectance measurements were made separately of a smooth silver film on a glass slide. The proportionality between the PA signal and absorptance determined for these smooth silver films was found to be good over the range of angles of incidence. This response constant was used to derive absorptance values of the diffraction grating from the PA signal.

III. RESULTS AND ANALYSIS

Photoacoustic signals from the diffraction grating are presented in Fig. 1 as a function of incidence angle for p- and s-polarized incident light. The various curves are for different azimuth angles θ of ruling orientation relative to the plane of incidence. The right ordinates of the figures give absorptances determined from the response constant obtained in the manner described above. For $\theta = 90°$, the absorptance curve for p-polarized light exhibits sharp peaks due to excitation of surface plasmons at three discrete angles of photon incidence, whereas no structure is found in the absorptance curve for s-polarized light. As was mentioned above, some of the surface plasmons excited in the diffraction grating may decay into photons in a certain direction for each diffracted order, and the remaining plasmons are absorbed internally in the metal coating. The photoacoustic data presented in Fig. 1 are a direct measurement of this internal dissipation of surface plasmons and represent the actual absorption of incident photon energy. The inability of s-polarized photons to excite surface plasmons in the case of $\theta = 90°$ is understood as due to absence of an electric field parallel to the grating vector. For $90° > \theta > 0°$, structures due to plasmon excitation appear in both absorptance curves for p- and s-polarized light. It is seen in Fig. 1 that, as θ is varied from 90° to 0°, the plasmon resonance angles shift systematically to higher incidence angles. Simultaneously the absorptance of the three plasmon peaks varies drastically with no significant change in the absorptance in the regions away from the resonance angles. For $\theta = 0°$, the plasmon peaks disappear from the absorptance curve for p-polarized light, whereas they remain in the curve for s-polarized light. In what follows, we compare these experimental results with predictions from relevant theories.

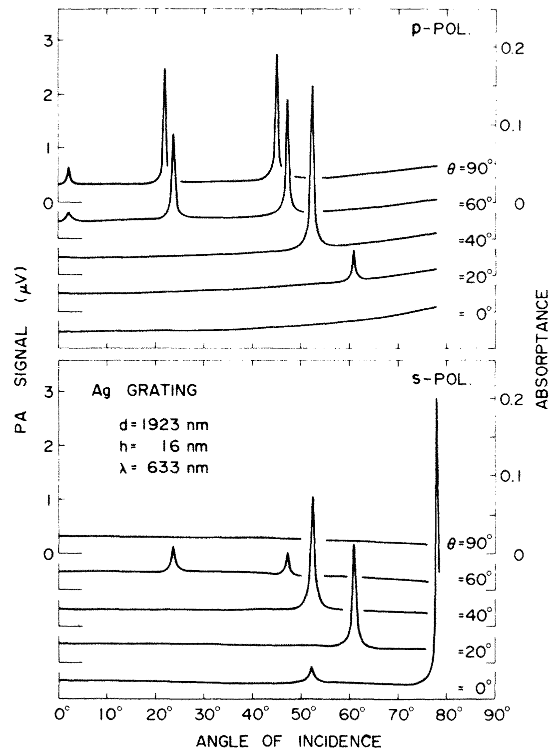

FIG. 1. Plasmon resonance absorption in a silver-coated diffraction grating for p- and s-polarized photons as a function of incident angles for various azimuth angles θ of ruling orientation relative to the plane of incidence. d is the grating constant, h is the groove depth measured from the mean surface, and λ is the photon wavelength.

The plasmon resonance condition in a diffraction grating is given by

$$\vec{k}_{sp} = \vec{k}' + n\vec{g} ,$$

where $\vec{k}_{sp}$ is the wave vector of surface plasmon, $\vec{k}'$ is the projection of wave vector of incident photon on the grating surface, $\vec{g}$ is the reciprocal grating vector, and $n = \pm1, \pm2, \pm3, \ldots$. For example, $\vec{k}_{sp}$, composed of $\vec{k}'$ and

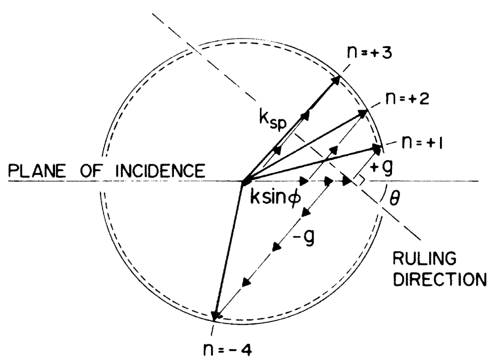

FIG. 2. Surface plasmon wave vector, $\vec{k}_{sp}$, in a diffraction grating composed of the component of the incident photon wave vector parallel to the grating surface, whose absolute value is equal to $\vec{k}\sin\phi$, and the grating vector $\vec{g}$ or its multiples, where k is the wave number of the incident photon and ϕ is the angle of incidence.

$\vec{g}$ in the momentum plane parallel to the grating surface, is presented graphically in Fig. 2 for the case of the present diffraction grating at $\theta=40°$. $|\vec{k}'|$ is represented in the figure by $k\sin\phi$, where k is the incident photon wave number and ϕ is the angle of incidence. The radii of the solid and dashed circles are equal to $|\vec{k}_{sp}|$ and $\vec{k}$, respectively, and hence the inside of the dashed circle corresponds to the radiative region. $|\vec{k}_{sp}|$ may be given by $|\vec{k}_{sp}|=k[\epsilon/(\epsilon+1)]^{1/2}$ if the effects of grating structure on the dispersion relation of surface plasmon are ignored, where ϵ is the dielectric function of the silver coating. In the case of $\theta=40°$ given in Fig. 2, there are four resonance angles corresponding to $n=+1$, $+2$, $+3$, and -4. Plasmons excited at each resonance angle have the propagation vectors $\vec{k}_{sp}$ in different directions. For the special case of $\theta=0°$, two surface plasmons with $n=\pm i$ whose propagation vectors are symmetric with respect to the plane of incidence are excited simultaneously at each resonance angle.

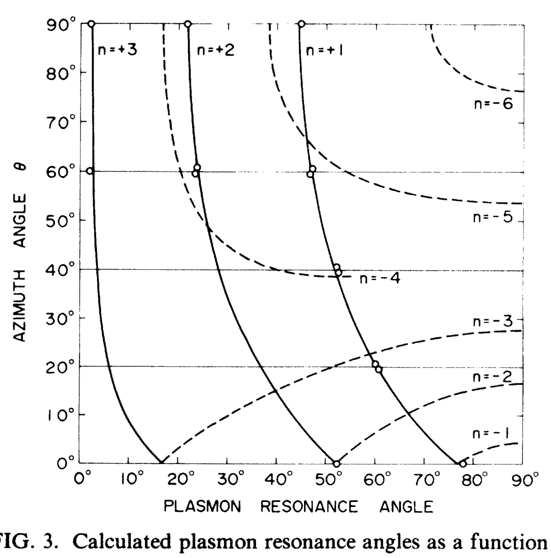

FIG. 3. Calculated plasmon resonance angles as a function of the azimuth angle θ of ruling orientation relative to the plane of incidence. Open circles represent the resonance angles observed in the experimental results in Fig. 1.

The resonance angles calculated from the resonance condition given above are presented in Fig. 3 as a function of the ruling orientation θ and are compared with the experimental observations presented in Fig. 1. The experimental resonance angles are seen to agree well with the calculated ones for $n=+1$, $+2$, or $+3$. The plasmon peaks in Fig. 1 may therefore be assigned to $n=+1$, $+2$, and $+3$, in order from higher to lower resonance angle. Some of the resonance angles observed are found to deviate slightly from the calculated ones, indicating a change of the surface plasmon wave number in the diffraction grating from that in the smooth surface.[23] We will discuss this further below.

Next, we examine the results of the absorptance values at the resonance angles presented in Fig. 1. Theoretical treatments of photoabsorption in diffraction gratings have been studied by many authors,[24–31] most of whom have calculated diffraction efficiency curves as a function of angle of photon incidence. McPhedran and Maystre[27] have used integral equations to explain the experimental results of plasmon resonance absorptions observed by Hutley and Bird[11] for a metal-coated holographic grating with a relatively deep groove profile. For shallow diffraction gratings, Heitmann[32] employed perturbation theory for light scattering, due to Kröger and Kretschmann,[33] obtained as a first-order solution of the equation in terms of h/λ, where h is the groove depth and λ is the incident photon wavelength. Heitmann found good agreement between theory and experiment for weakly modulated gratings if grating anomalies were avoided. Recently, Elson and Sung[34] have derived expressions for photoabsorption in rough surfaces, obtained to first-order of h/λ. Their expressions were shown to reproduce plasmon resonance absorptions in rough metal surfaces. Since for our diffraction grating $h/\lambda=0.025$, their expressions were expected to be applicable, so we used them to calculate plasmon resonance absorptances measured as a function of ruling orientation θ.

For the sake of simplicity and due to a lack of exact knowledge of the groove parameters of our diffraction grating, we have assumed that the groove profile was sinusoidal. Within the regime of the first-order approximation, this assumption restricted transfer momenta allowed in the grating surface to be $\pm\hbar\vec{g}$, and the surface structure factor which was given by the Fourier transform of the roughness correlation function was composed of two δ functions in the plane of transfer momentum, implying that only $n=+1$, and $n=-1$ plasmons were possible, contrary to the experimental results of Fig. 1. Calculations were made of the plasmon resonance absorptances at the theoretical resonance angles by using literature values[20] of the optical constants of silver and a groove depth $h=10$ nm. The results for p- and s-polarized incident light are plotted in Fig. 4 as a function of ruling orientation θ. The peak absorptances of $n=-1$ plasmons, which can be excited only for $4.3>\theta\geq 0°$ (see Fig. 3), are too small to plot in the figure in the case of p-polarized light. For comparison, experimental values of the peak absorptances in Fig. 1 are plotted in Fig. 4 after subtracting the background absorptances.

Agreement between theoretical and experimental peak absorptances for $n=+1$ plasmons is generally satisfactory, except for the results with p-polarized light at $\theta=60°$

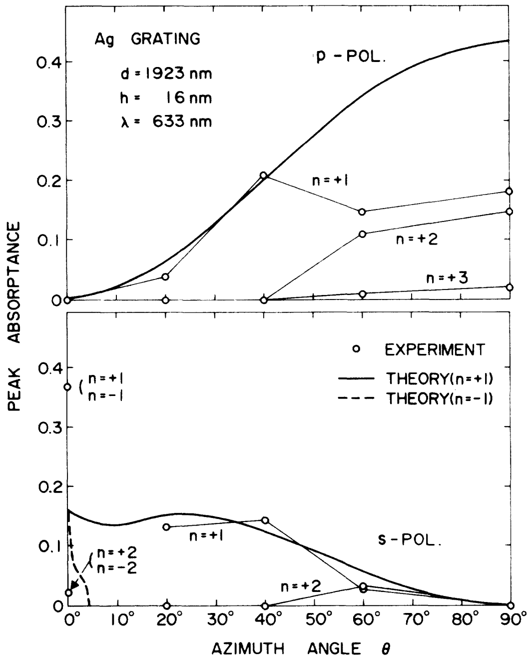

FIG. 4. Peak absorptances at plasmon resonance angles for p- and s-polarized photons as a function of the azimuth angle θ of ruling orientation relative to the plane of incidence. The theoretical values are calculated for groove depth $h = 10$ nm assuming sinusoidal groove profile.

and 90°, where significant discrepancies occur. However, it is seen that the deficit in the experimental values is compensated for by the appearance of the $n = +2$ and $+3$ plasmons in experimental results. This may be understood by remembering that the grating groove profile was assumed to be sinusoidal for the calculations. If the surface structure factor has a series of higher components of transfer momentum due to deviation from a sinusoidal groove profile, a redistribution of plasmon resonance absorptance should occur between the peaks corresponding to $|n| = 1$ and $|n| > 1$. This is seen in the results in Fig. 4. A similar redistribution of resonance absorptances is found in the results for s-polarized light at $\theta = 60°$. As was mentioned before, the peak absorptances observed with s-polarized light at $\theta = 0°$ are composed of two degenerated plasmons corresponding to $n = \pm i$, where i is an integer. The observed absorptance for $n = \pm 1$ plasmons is indeed nearly twice that of the calculated value.

In the case of plasmon resonance in a diffraction grating in which two surface plasmons propagating in different directions are excited simultaneously, a splitting of the plasmon resonance peak is generally expected.[35] The splitting stems from coupling of the two plasmon wave vectors mediated by the grating vector, which allows one surface plasmon to be scattered into the other in the grating surface. For the $n = \pm i$ plasmons for the ruling orientation $\theta = 0°$, the momentum transfer necessary for this scattering was $2i\hbar\vec{g}$. In our measurement of the plasmon peaks for $\theta = 0°$, no splitting was observed, indicating that the wave-vector coupling between the two plasmons was weak.

The value of the groove depth, $h = 10$ nm, used in the present calculation is significantly smaller than the experimentally determined value $h = 16$ nm. The calculated absorptance values are proportional to h^2 and thus are rather sensitive to the value of h used. They also depend on the values of the optical constants of silver used. We have made calculations using several different literature values of the optical constants of silver. Results similar to those plotted in Fig. 4 were obtained for $h = 10 \sim 12$ nm, which were consistently smaller than the experimental value. One reason for this discrepancy is that the first-order theory for photoabsorption does not include roughness-induced radiative relaxation of surface plasmons which is a second-order process. The observed plasmon resonance absorptions were due to plasmons which dissipated nonradiatively and therefore should be less than predicted from the first-order theory, thus giving a value of h smaller than the experimentally determined value.

IV. DISCUSSION

Recently, Maradudin[35] has suggested that studies of surface plasmons whose propagation vectors are not perpendicular to the ruling of diffraction grating may be of importance in connection with surface plasmons which can exist along the apex of a dielectric wedge. The plasmons excited in the present study were indeed propagating in different directions with respect to the ruling. Experimentally, it is important to determine the wave number of surface plasmons as a function of the propagation direction relative to the ruling. We have determined the wave number of each surface plasmon observed in the experimental data in Fig. 1 from the resonance angles observed. No appreciable directional dependence was found, however, in the results beyond the experimental uncertainty. A further study of this directional dependence of plasmon wave vector is now being undertaken by using diffraction gratings having various groove depths.

The optical properties of randomly or deterministically rough surfaces have been studied for many years. Experimentally, conventional optical techniques have restricted most studies to measurements of light scattering or reemission of photons from rough surfaces. In contrast to this, the present photoacoustic technique probes changes of internal energy occurring inside rough surfaces due to absorption of incident photons and thus opens a new experimental approach to the problem. The technique requires relatively simple experimental equipment and may be extended to other spectral regions. Limitation may arise, however, in the region of higher photon energies, where photochemical reactions including photoelectron emission and defect formation by incident photons have to be taken into account in the interpretation of photoacoustic data. Photochemical events could provide new channels of energy deposition and dissipation which do not contribute to heat production. For the silver sample used in the present study, the work function was much higher than the incident photon energy, and the possibility of photoelectron emission may be dismissed.

In our interpretation of the photoacoustic data presented above, we have employed the Rosencwaig-Gersho theory[1,19] of PA signal generation from solid samples, which assumes a smooth sample surface. The diffraction grating used in the present study was very shallow (ratio of the groove depth to the grating constant h/d was 0.0083), and the groove depth $h=16$ nm was smaller than the thermal diffusion lengths of both silver and air by a factor of 10^{-4}. The surface of our diffraction grating can therefore be considered to be thermally smooth.

In conclusion, we have measured plasmon resonance absorptions in a diffraction grating as a function of angle of ruling orientation relative to the plane of incidence. The results of the absorptance change as a function of ruling orientation were found to be consistent with predictions from the first-order perturbation theory of roughness-induced photoabsorption. A discrepancy was found, however, between the absorptance values determined experimentally and the values calculated from the first-order theory by using the value of groove depth determined experimentally from the diffraction intensity. This discrepancy was interpreted as due, in part, to roughness-induced radiative relaxation of surface plasmons which was not included in the first-order theory.

ACKNOWLEDGMENTS

This research was sponsored in part by the Office of Health and Environmental Research, U. S. Department of Energy, under Contract No. W-7405-eng-26 with the Union Carbide Corporation.

[1]For example, see A. Rosencwaig, *Photoacoustics and Photoacoustic Spectroscopy* (Wiley, New York, 1980).

[2]For example, M. A. Biondi, Phys. Rev. 96, 534 (1954); M. A. Biondi and A. I. Guobadia, Phys. Rev. 166, 667 (1968); W. Kasper and U. Kreibig, Surf. Sci. 69, 619 (1977).

[3]T. Inagaki, K. Kagami, and E. T. Arakawa, Phys. Rev. B 24, 3644 (1981).

[4]T. Inagaki, K. Kagami, and E. T. Arakawa, Appl. Opt. 21, 949 (1982).

[5]T. Inagaki, Y. Nakagawa, E. T. Arakawa, and D. Aas, Phys. Rev. B 26, 6421 (1982).

[6]For example, see H. Raether, *Excitation of Plasmons and Interband Transitions by Electrons* (Springer, Berlin, 1980), pp. 116–171.

[7]Y.-Y. Teng and E. A. Stern, Phys. Rev. Lett. 19, 511 (1967).

[8]R. H. Ritchie, E. T. Arakawa, J. J. Cowan, and R. N. Hamm, Phys. Rev. Lett. 21, 1530 (1968).

[9]J. J. Cowan and E. T. Arakawa, Z. Phys. 235, 97 (1970).

[10]M. C. Hutley, Opt. Acta 20, 607 (1973).

[11]M. C. Hutley and V. M. Bird, Opt. Acta 20, 771 (1973).

[12]C. E. Wheeler, E. T. Arakawa, and R. H. Ritchie, Phys. Rev. B 13, 2372 (1976).

[13]I. Pockrand, J. Phys. D 9, 2423 (1976).

[14]M. C. Hutley and D. Maystre, Opt. Commun. 19, 431 (1976).

[15]W. Rothballer, Opt. Commun. 20, 429 (1977).

[16]For example, J. C. Tsang, J. R. Kirtley, and J. A. Bradley, Phys. Rev. Lett. 43, 772 (1979); A. Girlando, M. R. Philpott, D. Heitmann, J. D. Swalen, and R. Santo, J. Chem. Phys. 72, 5187 (1980); A. Adams, J. Moreland, and P. K. Hansma, Phys. Rev. B 25, 3457 (1982).

[17]R. W. Wood, Philos. Mag. 4, 396 (1902).

[18]I. Pockrand and H. Raether, Opt. Commun. 18, 395 (1976).

[19]A. Rosencwaig and A. Gersho, J. Appl. Phys. 47, 64 (1976).

[20]P. B. Johnson and R. W. Christy, Phys. Rev. B 6, 4370 (1972).

[21]J. F. McClelland and R. N. Kniseley, Appl. Phys. Lett. 28, 467 (1976).

[22]For example, see K. Heihoff, J. Pelzl, N. Croitoru, and P. Cornaz, *Digest of Second Topical Meeting on Photoacoustic Spectroscopy* (Optical Society of America, Washington, D. C., 1981), TuB-13.

[23]For example, see A. J. Braundmeier and E. T. Arakawa, J. Phys. Chem. Solids 35, 517 (1974); I. Pockrand, Phys. Lett. 49A, 259 (1974); D. Heitmann, J. Phys. C 10, 397 (1977).

[24]A. Hessel and A. A. Oliner, Appl. Opt. 4, 1275 (1965).

[25]J. Hägglung and F. Sellberg, J. Opt. Soc. Am. 56, 1031 (1966).

[26]D. Maystre, Opt. Commun. 6, 50 (1972); 8, 216 (1973).

[27]R. C. McPhedran and D. Maystre, Opt. Acta 21, 413 (1974).

[28]D. Maystre, Opt. Commun. 17, 196 (1976).

[29]D. Maystre, and M. Nevière, J. Optics (Paris) 8, 165 (1977).

[30]K. Utagawa, J. Opt. Soc. Am. 69, 333 (1979).

[31]G. M. Whitman, D. M. Leskiw, and F. Schwering, J. Opt. Soc. Am. 70, 1495 (1980).

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

[33]E. Kröger and E. Kretschmann, Z. Phys. 237, 1 (1970).

[34]J. M. Elson and C. C. Sung, Appl. Opt. 21, 1496 (1982).

[35]A. A. Maradudin, in *Surface Polaritons*, edited by V. M. Argranovich and D. L. Mills (North-Holland, Amsterdam, 1982), Chap. 10.