Photoacoustic observation of nonradiative decay of surface plasmons in silver

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Photoacoustic observation of nonradiative decay of surface plasmons was made on the plasmons excited at a silver-air interface by the attenuated-total-reflection method. Analysis made in conjunction with simultaneously measured optical absorptance data allowed us to separate the radiative and nonradiative relaxations and determine their relative probabilities.

Nonradiative surface plasmons, which propagate as polarization waves along a metal surface with phase velocities less than that of light in vacuum are unable to decay directly into photons, unless roughness is present at the surface.[1] The plasmons undergo nonradiative decay first into single-electron excited states, after which emission of photoelectrons may occur[2] if the plasmon energy exceeds the work function of the metal. The rest of the single-electron excited states relax nonradiatively through electron-electron and electron-phonon collisional processes and eventually degrade into tiny quanta of lattice energy. This main decay channel of the nonradiative surface plasmons has been difficult to study by conventional experimental methods, because the decay products are in the form of heat.

The photoacoustic technique[3] as used for solid samples is based on an effect which may be observed by illuminating a sample placed in a sealed gas-filled cell by a chopped monochromatic photon beam. Absorption of photons in the sample produces a periodic heat generation through nonradiative relaxation of the excited states, and the subsequent heat flow from the sample to the gas causes a periodic pressure variation in the cell which may be detected by a microphone exposed to the gas. The photoacoustic method is thus capable of probing nonradiative deexcitations which follow a variety of elementary excitations in matter. In this report we present the first experimental results of photoacoustic observation of nonradiative decay of surface plasmons excited at a Ag-air interface. The results obtained are analyzed in conjunction with simultaneously measured optical reflectance and transmittance data.

The cross section of an ATR (attenuated-total-reflection) photon-plasmon coupler[4] equipped with a photoacoustic cell is shown in Fig. 1. A 2×18-mm^2 slip of 34-nm-thick Ag film was deposited on the hypotenuse surface of a strain-free 45° glass prism by vacuum evaporation. A photoacoustic cell consisting of a transparent polycarbonate frame, a glass exit window and a tiny electret microphone (Prima EM-60) was then placed in an air-tight manner on the prism surface. The thickness of the air-filled cavity formed above the Ag film was 1 mm. By illuminating the Ag film from the prism side with a chopped parallel beam of 632.8-nm photons from a 1-mW He-Ne laser, nonradiative surface plasmons were excited at the Ag-air interface. Photoacoustic signals generated in the cavity was measured as a function of the angles of incidence of both *p*- and *s*-polarized photons and their chopping frequencies between 100 and 800 Hz, using an experimental setup which employed a mechanical light chopper and a lock-in amplifier.

Prior to setting on the prism coupler, our cell was checked for the photoacoustic response by measuring the output signal versus incident photon intensity using a light attenuator. A black rubber sample was illuminated through the exit window of the cell with the chopped photon beam of variable intensity. The signal amplitude was found to be proportional to the incident photon intensity at each chopping frequency over the signal range observed in the present experiments. Since a prism was used for our photon-plasmon coupler, the beam was incident on slightly

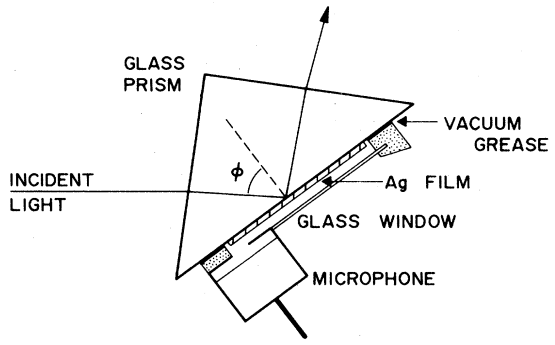

FIG. 1. Schematic cross-sectional view of the ATR photon-plasmon coupler equipped with a photoacoustic cell.

different portions of the Ag film as the angle of incidence was varied. However, no appreciable difference was found in the signal amplitude obtained by illuminating the different portions of the sample through the exit window. The background signal amplitudes measured with the blank prism coupler were negligible at all chopping frequencies.

Simultaneously with the photoacoustic measurements, the p- and s-polarized photon intensities both reflected from and transmitted through the prism coupler were measured. After being corrected for the reflection losses at the prism and the exit window surfaces, these data were used to determine the optical reflectance R and the transmittance T for the two boundary system of prism-Ag-air, from which the absorptance $(1-R-T)$ in the Ag film was determined as a function of the angle of incidence.

The results of R_p presented in Fig. 2(a) as a function of the angle of incidence ϕ exhibits the well-known sharp dip due to plasmon excitation at the angles just above the critical angle (41.30°). Correspondingly, strongly enhanced photoacoustic signals were observed with the cell on the prism coupler

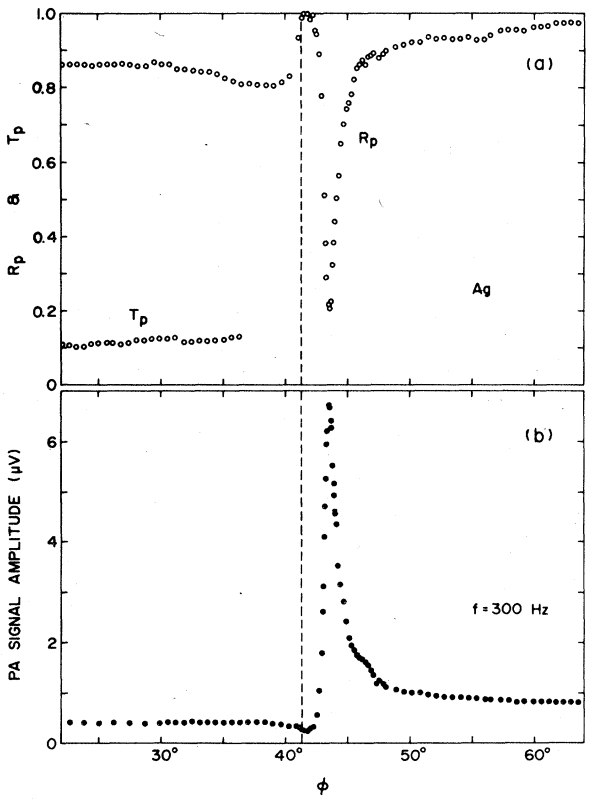

FIG. 2. (a) Reflectance R and transmittance T for p-polarized photons as a function of the angle of incidence ϕ. (b) Photoacoustic signal amplitude obtained with p-polarized photons at the chopping frequency $f=300$ Hz as a function of the angle of incidence ϕ. Dashed lines indicate the position of the critical angle.

when p-polarized photons were incident at the angles for which the plasmon dip in R_p occurred. A representative data set taken at the chopping frequency $f=300$ Hz is shown in Fig. 2(b). This signal enhancement at the plasmon resonance angle is a direct observation of the nonradiative decay of surface plasmons into heat. The results obtained at other chopping frequencies (f) were essentially the same as that shown in Fig. 2(b), except for a constant factor which showed an approximate $1/f$ dependence. The transmittance T at angles just below the critical angle were not measured because the cell frame interfered with the transmitted photon beam and at angles above the critical angle no light was transmitted.

In the photoacoustic measurements described above, the depth profile of the energy distribution in the film sample immediately after absorption of photons depends strongly on the angle of incidence. A previous calculation[2] of the energy-density profile in an ATR system similar to the present one shows that, for normal incidence, the energy density in the metal film decreases nearly exponentially away from the surface of incidence. At the plasmon resonance angle, however, it is reversed and has a profile very similar to that produced by photons incident from the air side of the film. On the other hand, the thermal diffusion length[5] μ of Ag defined by $\mu=(k/\pi f\rho C)^{1/2}$ at, for example, $f=300$ Hz is evaluated to be 4.28×10^5 nm, where k is the normal conductivity, ρ is the density, and C is the specific heat of Ag. Our 34-nm-thick Ag film is therefore "thermally very thin" at the present chopping frequencies. Also this diffusion length is larger than the penetration depth of the incident photons in Ag by a factor of 10^4. For such a metal sample placed between glass and air, the basic theory for photoacoustic signal generation in solids due to Rosencwaig and Gersho[5] and other modifications of this theory[6] predict that the signal amplitude is proportional to the total amount of absorbed energy and, hence, to the absorptance in the sample, and does not depend on the initial energy distribution. To apply this prediction to our photoacoustic system, the assumption is made that the excited states created in the sample at any angles of photon incidence relax nonradiatively and contribute equally to the signal generation. This is the case of the present experiments in which the absorptance observed as a function of the angle of incidence is due either to plasmon creation or to intraband excitation of the conduction electrons in Ag, both of which deexcite nonradiatively. Since the incident photon energy, 1.96 eV, is much smaller than the reported values,[7] 4.5 ± 0.2 eV of the work function of Ag, the possibility of photoelectron emission from these excitations may also be ignored if these values are valid for our Ag sample. Thus, the photoacoustic signal amplitude obtained as a function of the angle of incidence may be expected to be proportional to the

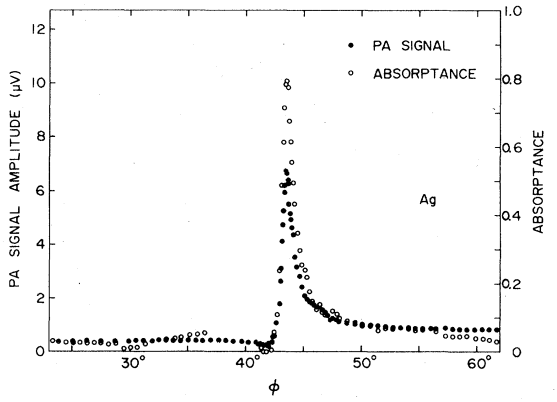

FIG. 3. Comparison between the photoacoustic signal amplitude and the absorptance for p-polarized photons as functions of the angle of incidence ϕ.

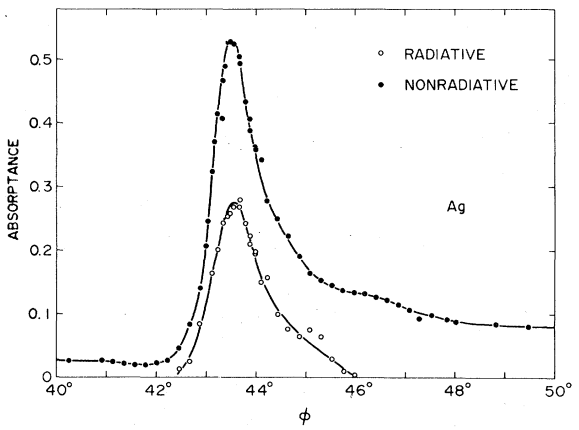

FIG. 4. Absorptance for p-polarized photons as a function of the angle of incidence ϕ for radiative and nonradiative relaxations.

absorptance values.

Comparison is made between the photoacoustic and the absorptance data for p-polarized photons in Fig. 3, where the former data are normalized so that the values in the angle range outside the plasmon resonance agree with the absorptance values. The overall behavior of the photoacoustic data is, indeed, found to agree well with the absorptance data. With the same normalization constant, we found a good agreement between the photoacoustic and the absorptance data for s-polarized photons. It is seen, however, that the photoacoustic data in Fig. 3 exhibit an appreciably weaker signal in the plasmon resonance region as compared with the absorptance values, indicating that a part of the absorbed energy is missing in this particular region of the angle of incidence. Since the relaxation times of the surface plasmon and the intraband excitation in Ag, estimated from the optical constants to be of the order of 10^{-13} and 10^{-14} sec, respectively, are too short to affect[8] the signal generation at the present chopping frequencies, the missing energy cannot be explained by the relaxation times. The missing part of the absorbed energy is thus attributed to the radiative decay[1,9] of nonradiative surface plasmons by the roughness in our evaporated Ag film, although the question concerning the true value of the work function of our Ag sample, which is sensitive to surface conditions, remains to be answered. At the plasmon resonance angles and only at those angles, in fact, scattered plasmon radiations from the Ag film could be observed through the exit window on the prism coupler, as has been observed before by many authors[9] for evaporated Ag films.

The absorptances for p-polarized photons observed at each angle of incidence are divided in Fig. 4 into two parts, one which contributed to the photoacoustic signal by decaying nonradiatively into heat, and one which escaped from the sample by decaying into photons or into emission of photoelectrons without contributing to the photoacoustic signal. It is seen that at the plasmon resonance angle the ratio between these two parts of the absorbed energy is roughly two, implying that, for the present Ag sample, the absorbed radiative quantum yield at the resonance angle is roughly 0.3.

In conclusion, nonradiative decay of nonradiative surface plasmons was observed photoacoustically. By performing photoacoustic and optical measurements simultaneously on a photon-plasmon coupler, we were able to separate the radiative and nonradiative relaxations of the surface plasmons and determine their relative decay probabilities. Extension of the present technique to other types[1] of surface excitation by the ATR method is straightforward.

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[1]See for review, for example, A. Otto, in *Optical Properties of Solids—New Developments,* edited by B. O. Seraphin (North-Holland, Amsterdam, 1976), Chap. 13.

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