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Coupled surface plasmons excited by photons in a free-standing thin silver film

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We report the first observation of coupled modes of nonradiative surface plasmons excited by photons in a free-standing thin metal flim. Excitation of these modes was achieved by introducing shallow periodic corrugations on the surfaces of a 44-nm-thick silver film, and the plasmon resonance absorption of photons was detected by a photoacoustic method.

It is well known theoretically[1-3] that nonradiative surface plasmons on the two surfaces of a thin metal film interfere with one another and set up two surface plasmon modes. The mode with a smaller wave number (the k^- mode) has a surface charge asymmetric with respect to the midplane of the film with the electric field predominantly normal to the film. The other mode with a larger wave number (the k^+ mode) has a symmetric surface charge with the electric field essentially parallel to the film. Experimentally, the dispersion of these modes has been studied rather extensively for the last two decades primarily by characteristic electron energy-loss measurements.[4] However, the dispersion in the small wave-number region (the retarded region) near the light line and the resonance width have been difficult to study due to the limited experimental accuracy stemming from instrumental resolution.

Recently, Fukui, So, and Normandin[5] have found that the lifetime and, hence, the propagation distance of the k^- mode evaluated from the dispersion relation increases as the film thickness t decreases. Subsequently, Sarid[6] has confirmed that the imaginary part of the wave number k $(=k_1+ik_2)$ goes to zero as t approaches zero. Since k_2 describes the rate of special damping, this mode was called the long-range surface plasmon (LRSP). This interesting property of the k^- mode results from the fact that the fraction of the electric field associated with this mode inside the film becomes small as t decreases, and, hence, the rate of internal dissipation also becomes small. This prediction has stimulated considerable interest in optical excitation[7-9] of the k^- mode and the use of this mode to enhance nonlinear optical interactions.[10-13]

Optical excitation of coupled surface plasmons was examined by Otto[14] soon after he demonstrated the prism method for optical excitation of nonradiative surface plasmons. He proposed a geometry consisting of a thin metal film bounded on both sides by identical dielectric layers and then sandwiched between two high-index prisms. However, experimental verification had not been made until very recently. Kuwamura, Fukui, and Tada,[7] Quail, Rako, and Simon,[8] and Craig, Olson, and Sarid[9] have made ATR (attentuated-total-reflection) measurements on systems similar to those proposed by Otto, removing the prism on one side of the film which proved to be unnecessary. As was predicted, these authors have observed a supernarrow resonance of the k^- mode with the angular width smaller by a factor of 10 than that of the single-surface mode observed with the ordinary Otto or Kretschmann geometries. The simplest system that exhibits coupled surface plasmons is a free-standing thin metal film. However, such a film is difficult to put into a prism geometry. In this Rapid Communication we report the first observation of coupled surface plasmons in a free-standing thin silver film excited by photons through grating coupling.[15]

The free-standing thin silver films with shallow periodic corrugations were made by evaporating silver onto a plastic replica grating.[16] Prior to evaporation of silver, the grooved side of the grating was covered with a thin collodion (cellulose nitrate) film by picking up the film floating on the surface of a water pool. The film was prepared by spreading a drop of collodion solution on the water surface and allowing the solvent to evaporate. After vacuum-evaporating silver on the collodion film, the grating was glued on an aluminum frame with a 2×10-mm^2 aperture and then immersed into a pool of amylacetate, a solvent for collodion. The collodion film dissolved away within a few hours, leaving a corrugated silver film separated from the plastic grating. The silver film on the frame was carefully lifted from the pool of amylacetate and then allowed to dry. The groove spacing d of the corrugated silver film thus fabricated was determined from the diffraction angles of He-Ne laser light. The corrugation amplitude h was estimated[16] from the first-order diffraction intensity of s-polarized light at normal incidence measured on both the incident and the exit sides of the film in case the film was semitransparent.

We have already shown[16,17] that the photoacoustic (PA) method, which measures photoabsorption by probing heat generation occurring inside the sample under study, is a useful, convenient, experimental technique for investigation of plasmon resonances in diffraction gratings. For the present study, we have employed this same experimental technique. The free-standing thin film sample was placed in an air-filled nonresonant PA cell[18] equipped with an electret condenser microphone with the grooves perpendicular to the plane of photon incidence. A 633-nm-photon beam from a 1-mW He-Ne laser was directed to the film sample through a glass window after being chopped at 300 Hz, and the PA signal was measured as a function of the angle of incidence. Details of the PA cell and the signal detection system have been described earlier.[16] Since the silver films studied were thinner by a factor of 10^4 than the thermal diffusion length, the measured signals are known to be proportional to the absorptance,[16,18] the fraction of the incident photon energy dissipated in the film.

The PA signals obtained with p-polarized incident photons for 106- and 44-nm-thick free-standing films are presented in Fig. 1 as a function of the angle of incidence. The corrugation amplitudes h of these films were 21 and 17 nm, respectively, and their groove spacings d were 1899 nm. The 106-nm-thick film shows sharp absorption peaks due to plasmon resonances at three different angles, 48°, 24°, and 4°. These peaks correspond to the $m=+1$, $+2$, and $+3$ resonances, respectively, given by the resonance condition[16] $k_1=(\omega/c)\sin\phi+m(2\pi/d)$, where ϕ is the angle of incidence. These results are similar to those observed for a single-surface system of a silver-coated shallow diffraction grating.[16] The 44-nm-thick free-standing film exhibits the plasmon resonance structures in the same angular regions as shown by the 106-nm-thick film. Each absorption peak, however, splits into two peaks, one at a higher resonance angle and the other at a lower resonance angle. This splitting is due to the excitation of coupled surface plasmons which result from the interaction of plasmon waves on the two sides of the film. In the 106-nm-thick film, the overlap between the plasmon fields on the two sides of the film was small, and, hence, a highly decoupled mode resulted, similar to that on a single surface.

It is seen that the peak at lower resonance angle (the k^- mode) is considerably narrower than the peak at higher resonance angle (the k^+ mode), exhibiting the long-range propagation property as pointed out by Fukui *et al.*[5] and Sarid.[6] Also, the angular shifted of this k^- mode relative to the single-surface mode, which is represented by the 106-nm-thick film data, is only one-half of the shift of the k^+ mode. These differences between the two split modes are seen clearly in both the $m=+1$ and $+2$ resonances. Note that the shape of the k^+ resonance is highly asymmetric, whereas that of the long-range k^- mode is nearly symmetric.

The presence of periodic corrugations on an infinitely thick metal surface is known[19] to change both the dispersion and the damping of surface plasmons from what they are on a planar metal surface. For shallow corrugations with fixed groove spacing, the propagation constant k_1 and the damping constant k_2 both increase as the corrugation amplitude h increases. For a two-surface film system, the k^+ and k^- modes have quite different field patterns inside the film. Therefore, the effects of corrugation may not be the same on the k^+ as on the k^- mode. From the observed resonance angles the propagation constants k_1 for the k^+ and k^- modes and the single-surface mode were found to be 1.11, 1.05, and 1.07, respectively, in units of (ω/c). These values are significantly larger than those given by the dispersion relation[3] for a free-standing *planar* silver film, which are presented in Fig. 2(a) as a function of the film thickness t. It is seen that the observed separation in the k_1 value between the k^+ and k^- modes is nearly twice the calculated separation. On the other hand, from the observed angular width at the half maximum, the resonance widths Δk_1 for the coupled and single-surface modes were found to

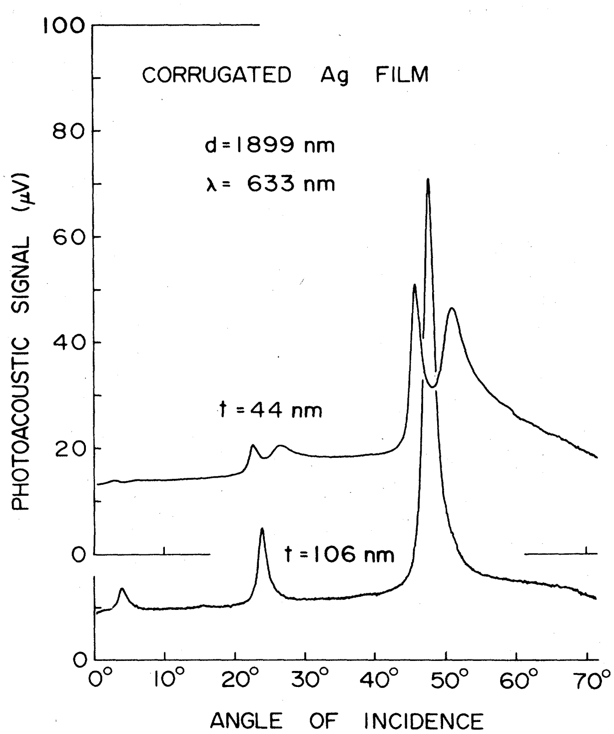

FIG. 1. Photoacoustic signal observed with p-polarized 633-nm photons for 106- and 44-nm-thick free-standing corrugated silver films as a function of the angle of incidence. The corrugation amplitudes were 21 and 17 nm, respectively, and the groove spacing $d=1899$ nm was common to the two films.

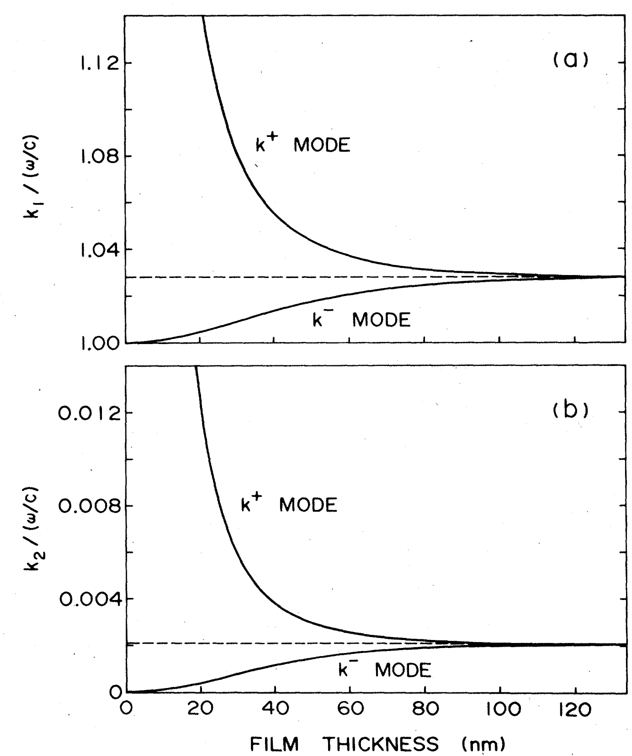

FIG. 2. Propagation constant k_1 and damping constant k_2 for the k^+ and k^- modes of coupled surface plasmons in a free-standing *planar* silver film calculated at the frequency corresponding to the photon wavelength $\lambda=633$ nm in free space as a function of the film thickness. The literature values of the optical constants of silver due to Johnson and Christy (Ref. 22) were used in this calculation.

be 0.063, 0.025, and 0.023, respectively, in units of (ω/c). These values are roughly one order of magnitude larger than the calculated damping constant k_2 presented in Fig. 2(b). Note that the observed resonance width of the k^- mode is comparable to that of the single-surface mode, indicating that the range of propagation of the k^- mode observed in our free-standing corrugated film is not too different from that of the single-surface mode. In addition to the periodic corrugation, microscopic random roughness and a slight periodic variation in the film thickness were difficult to eliminate from the film sample made by the method described above. These imperfections could be responsible for the observed modification of the propagation and damping of the coupled surface plasmons.

Recently, Farias, Maradudin, and Celli[20] have studied theoretically the dispersion of coupled surface plasmons in a periodically corrugated metal film. Their treatment of the problem, however, was made neglecting retardation and, hence, is not applicable to the present experimental results obtained in the retarded region. Finally, we note that Pockrand[21] has observed a coupling between surface plasmons excited by the prism method on the boundaries of a thin metal film. Since in his experiment the film was bounded on one side by a dielectric spacer layer and on the other side by air, the plasmons had two different propagation constants. Therefore, in order for the two plasmons to be coupled, it was necessary to introduce a periodic corrugation in the film, by which the propagation constant of the plasmon on the dielectric-side of the film was reduced to match that of the plasmon on the air side of the film. Thus, the creation of coupled surface plasmons was indirect.

In summary, coupled surface plasmons have been excited by photons for the first time in a free-standing thin silver film. Conversion of photons to surface plasmons was achieved by introducing a periodic corrugation in the film, which inevitably caused a significant modification of the dispersion and the damping of the excited coupled plasmons.

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