Optical Second-Harmonic Generation with Long-Range Surface Plasmons

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The first observation of enhanced optical second-harmonic generation due to excitation of the long-range surface plasmon is reported. When the fundamental mode of this plasmon is excited on both surfaces of a thin silver film bounded by a nonlinear quartz crystal and an index-matched liquid, the harmonic generation is over 2 orders of magnitude larger than that due to a single-boundary surface plasmon. Nonlinear excitation of the harmonic long-range surface-plasmon mode is also observed.

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The recent prediction[1] of the properties of a new long-range surface-plasmon (LRSP) mode on the two surfaces of a thin metal film bounded by index-matched dielectrics has stimulated theoretical interest in this new mode. In particular the applications to nonlinear optics of the large field enhancements[2] associated with the LRSP have received considerable attention. Excitation of the LRSP mode on semiconductors in the infrared region is predicted to produce large enhancements in the generation of three- and four-wave optical mixing processes[3] and increased nonlinear propagation lengths for surface modes.[4] Enhanced optical second-harmonic generation (SHG) due to the excitation of the surface-plasmon mode at the single boundary between a metal film and a nonlinear crystal has been studied.[5] Calculations for similar SHG experiments using the LRSP mode predict[6] additional enhancement factors of 4 orders of magnitude.

The first linear experimental demonstrations of the sharply resonant attenuated total reflectivity[7] and enhanced propagation length[8] of the LRSP have just recently been reported. In this Letter we now report the first observation of enhanced SHG due to excitation of the fundamental-mode LRSP in a thin silver film bounded by a noncentrosymmetric quartz crystal and an index-matched liquid. In addition we report the first observation of the nonlinearly excited harmonic LRSP with a p-polarized incident fundamental wave.

The long-range surface-plasmon mode is a transverse-magnetic electromagnetic wave propagating along both boundaries of a thin metal film bounded by two semi-infinite index-matched dielectric media.[1] The properties of the evanescent waves associated with a surface plasmon propagating on a semi-infinite metal/dielectric interface are well known.[9] As the metal layer thickness decreases in this case the evanescent waves from the two surfaces couple to form symmetric and antisymmetric (in electric field distribution) normal modes. The former is the short-range mode and the latter the long-range mode which has an enhanced surface-propagation decay length.

The reflected SHG with LRSP excitation may be easily calculated by following the procedure used for single boundary surface plasmons.[5] Consider a p-polarized electromagnetic wave incident from a high-index prism through a thin dielectric layer into a semiopaque metal film evaporated on a nonlinear crystal as shown in Fig. 1. The amplitude of the fundamental wave inside the crystal is determined by the appropriate linear Fresnel factor for the multilayer geometry.[10] The fundamental evanescent field in the nonlinear crystal drives a nonlinear polarization wave which radiates a reflected second-harmonic wave. The second-harmonic reflection coefficient R which is defined as the ratio of the reflected second-harmonic irradiance to the square of the fundamental irradiance has been computed in Ref. 6. For the appropriate angles of incidence there exist two poles in R which mark the excitation of a LRSP at the fundamental and harmonic frequency,

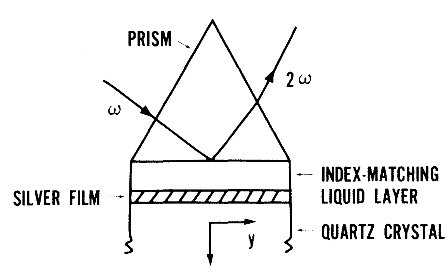

FIG. 1. Prism coupling arrangement for second-harmonic generation (SHG) with long-range surface plasmon (LRSP) mode. Crystal axes oriented as shown.

respectively. The theoretical calculation of R is performed with standard values for the optical constants of the prism, metal, crystal, and index-matching liquid.

The preparation of the prism/dielectric-layer/metal-film/crystal sample has been described in detail.[7] Briefly, a thin silver film whose thickness was determined to within 10% by a Sloan digital thickness monitor was evaporated on an X-cut quartz crystal. The crystal and metal film were mechanically pressed against the hypotenuse face of a high-index SF-59 coupling prism with an intervening layer of index-matched liquid. The thickness of the liquid layer was independently determined also to within 10% by observing interference fringes created by a He-Ne laser at angles of incidence below the critical angle for total reflection. The prism arrangement was mounted on a rotation stage which could be rotated in 0.02° increments.

The laser used for the SHG experiment was a passively mode-locked Nd glass laser whose output consisted of a 100-nsec train of approximately 15 mode-locked pulses with a total energy of 30 mJ, from which we estimate the maximum peak power per pulse to be approximately 100 MW over a circular area of 0.07 cm^2. This power level was attenuated by up to 3 orders of magnitude to prevent damage to the thin silver film. A glass beam splitter was used to direct a fraction of the beam into a fixed quartz sample for producing SHG in the monitor channel. The main beam after passing through series of rotatable polarizers was incident on the prism assembly with the X-cut quartz crystal oriented as shown in Fig. 1. The observed second-harmonic light was tested for correct polarization, wavelength, collimation, and most importantly the calculated 5° offset angle from the linearly reflected fundamental light due to the dispersion of the glass prism. SHG data were recorded digitally by means of a standard dual-channel arrangement.

To demonstrate the effect of a fundamental LRSP mode on SHG a 135-Å silver film was evaporated on the quartz crystal and the liquid layer was adjusted to 30 000 Å for near optimal coupling of the fundamental LRSP mode into the crystal. The result of this experiment is shown in Fig. 2 where the reflected SHG data are plotted on a logarthmic scale versus the interior angle of incidence measured at the base of the prism. The observed SHG changes dramatically by more than 4 orders of magnitude over a narrow angular interval of 0.2° because of the excitation of the fundamental LRSP. This sudden change in SHG is directly due to the linear enhancement of the LRSP mode field in the nonlinear crystal by a factor of 40 relative to the incident field. The solid curve shows the theoretical angular dependence of the second-harmonic reflection coefficient for the above values of liquid layer and metal film thicknesses. We note that a 10% variation in the choice of these latter parameters may produce an additional factor of 10 in the theoretical value of R. As has been pointed out previously[7,8] diffraction effects due to the finite width of the beam prevent ideal coupling to the LRSP and hence limit the maximum experimental value of R. The observed peak has been experimentally calibrated to the theory by comparing to the transmitted SHG in a C-axis quartz crystal. The dotted curve, which is displayed for comparison purposes only, shows the theoretical angular dependence of R for the case of excitation of the single-boundary surface plasmon.[5] This curve was calculated by setting equal to zero and 550 Å, respectively, the thicknesses of the liquid layer and silver film. The enhancement factor for the SHG due to the LRSP is over 2 orders of magnitude larger than that due to the single-boundary surface plasmon.

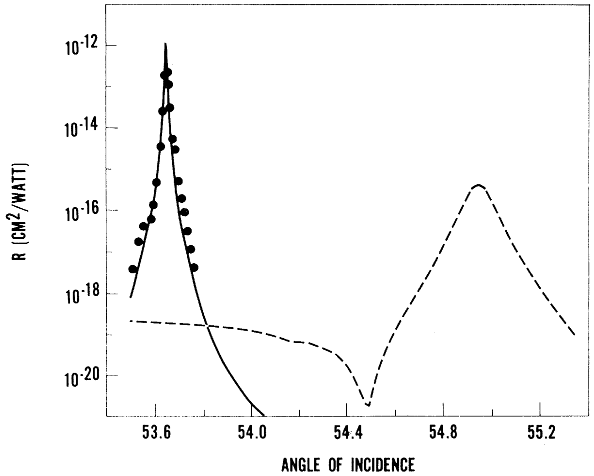

FIG. 2. The second-harmonic reflection coefficient, R, from multilayered system shown in Fig. 1, for the case of nearly optimal coupling to the fundamental LRSP mode, vs the interior angle of incidence. The experimental points are normalized to the theoretical solid curve as discussed in text. The dotted curve displays the case of a single-boundary surface plasmon for comparison purposes only.

To demonstrate the effect of the harmonic LRSP mode the arrangement was similar to that above except the silver film thickness was in-

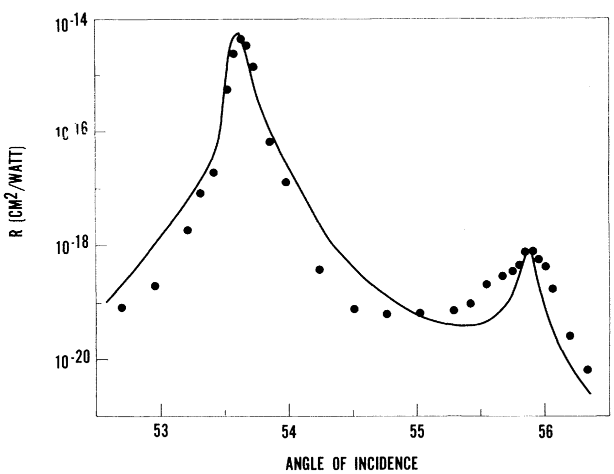

FIG. 3. The second-harmonic reflection coefficient, R, for the case of demonstrating coupling to both fundamental and harmonic LRSP modes, vs the interior angle of incidence.

creased to 185 Å and the liquid layer thickness was reduced to 10 000 Å. In this case the fundamental LRSP is overcoupled but coupling to the harmonic LRSP is enhanced. For the above quartz orientation, p-polarized SHG is produced by p-polarized fundamental radiation.[11] The results are shown in Fig. 3 where the first peak, which is due to the overcoupled fundamental LRSP, is broader and reduced in height relative to the peak due to the LRSP shown in Fig. 2. The second peak, due to the nonlinear excitation of the harmonic LRSP, is now clearly visible. Note that on the logarthmic scale this second peak rises by a factor of 10 above the nonresonant background SHG. The agreement between theory and experiment is quite good although the observed width of the second peak cannot be explained by any reasonable adjustment of the optical parameters. The normalization of the data to the theoretical curve is identical to that used in Fig. 1. This is the first observation of a nonlinearly excited surface-plasmon mode at a metal/nonlinear-crystal interface. In all previous experiments designed to illustrate nonlinear excitation of the surface-plasmon mode in silver[5] or aluminum[12] films with either p- or s-polarized input waves, the SHG from the metal alone dominated the observation.[13] In the present experiment with a relatively thin metal film, the dominant SHG is due to the nonlinear crystal while the SHG due to the metal surface is always at least 1 order of magnitude smaller.[14]

In conclusion we have observed a dramatic new nonlinear optical effect. The coupling of the LRSP mode into a quartz crystal produces an increase in the reflected SHG by more than 4 orders of magnitude over a narrow angular interval of 0.2°. This enhancement is over 2 orders of magnitude greater than the enhancement due to the single-surface plasmon mode. In addition the nonlinear excitation of the harmonic LRSP for a p-polarized incident wave has been achieved. These experiments demonstrate that excitation of the LRSP mode can now be applied to a broad class of nonlinear optical phenomena including three- and four-wave mixing experiments. The enhanced, localized nature of the antisymmetric field distribution associated with the LRSP mode will make this mode a useful new optical probe for studying metal/dielectric interfaces.

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