Second-harmonic generation and photoemission from silver

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We have observed photoemission induced by second-harmonic photons from a NH_3-covered Ag film in the attenuated-total-reflection configuration. The photoyield increases as the square of the laser intensity. The dispersion relation for the photoemission is identical with that for the surface-plasmon-polariton. The angular variations of the reflectance and of the photoyield are accurately described by standard Fresnel optics when dielectric constants close to those found in the literature and a reasonable value of the electron escape length are used. Photons from a pulsed dye laser with energies in the range 1.8–2.6 eV were used. Measurements of the reflectance and photoyield were made simultaneously.

INTRODUCTION

We have observed second-harmonic- (SH) induced photoemission from NH_3 covered Ag films in the attenuated total reflection (ATR) configuration. Optical constants determined from simultaneous measurements of ATR were used to relate the photoyield to a simple model of the absorption. In an ATR experiment, light is directed through a prism onto a metal film and the light reflected from the prism-metal interface is measured.[1,2] At angles above the critical angle the evanescent wave will couple into surface plasma oscillations on the metal surface if both energy and momentum conservation conditions are satisfied. When a surface-plasmon polariton (SPP) is excited, there is a minimum in the reflectance. At the same angle, photoemission will be enhanced as decay of the plasmon may excite a single electron above the surface barrier.

Callcott and Arakawa[3] made early measurements of photoyield from Al in an ATR system, at high photon energies but at intensities too low for second-harmonic generation (SHG). Rudolf and Steinmann[4] made similar measurements using 2.6-eV photons with an Al film and observed a SH-induced term. Hincelin[5] reported both photoemission and ATR from a thin cesiated Al film but his intensities were too low for SHG. Quail and Simon[6] have directly observed SH light generated at the prism-metal interface in total internal reflection (TIR) experiments on both Al and Ag thick films. In Ag there have been no previous experiments combining photoemission and ATR. Stuckless and Moskovits[7] have reported two-photon-induced photoemission from smooth and rough Ag films. Our measurements are the first to combine reflectance and photoyield measurements on Ag with the intensities necessary for SHG.

In the following section we discuss the experimental procedure and then present some of the data. In the final section the data are discussed.

EXPERIMENT

We use the Kretschmann configuration[2] for ATR measurements. Laser light is directed through the curved surface of a hemicylindrical prism onto a Ag film deposited onto the flat surface. The reflected light and photocurrent are simultaneously measured as the angle of incidence is varied. The anode also rotates so that it is always in the same position with respect to the photocathode. Our prisms are made from flint glass (SF-10 Schott Glass, index of refraction $n=1.744$) and from uv-grade quartz ($n=1.462$).

Light is provided by a Molectron pulsed dye laser operating at 11 Hz. The photoelectron signal is amplified by a modified Ortec 142PC preamplifier and fed to a Quanta Ray DGA-1 gated amplifier along with the reflectance signal from a photodiode. The two signals then go to a Macintosh II computer that uses National Instruments' LabView software and hardware.

The metal is evaporated onto a room-temperature substrate (prism) at a 10^{-7}-Torr base pressure. Measurements are made at room temperature in a different vacuum chamber with a 10^{-8}-Torr base pressure. All of our surfaces are initially exposed to air. Stable coverages of NH_3 are maintained by filling the chamber with controlled amounts of NH_3 gas. The yield increases with NH_3 pressure up to 2 Torr, then rapidly decreases; a monolayer must correspond to about 2 Torr. We have chosen NH_3 as an adsorbate because of our interest in liquid NH_3.[8]

The photoemission yield and reflectance are measured and recorded simultaneously as functions of the angle of incidence φ with a resolution of 19 points per degree. The angular scan is made at a rate of 0.320°/sec. Photon energies range from 1.89 to 2.6 eV. The Molectron pulsed dye laser provides a beam intensity of 0.1 mJ with a duration of about 10 nsec. With the laser beam focused to an area of 0.004 cm^2, the power level at the metal surface can reach up to 2.8×10^7 W/cm^2. At this power level, a second-harmonic electromagnetic wave may be generated.[6] For photon energies above 2.3 eV, we observe photoemission from the thin Ag films. According to other experimental results in our laboratory, the work function of a *smooth* silver film can be lowered to about 3.8 eV by adsorbed NH_3.

Intensities are given in terms of the output voltage of an Ealing photodiode. The value of 1.0 V in light intensi-

ty corresponds to a peak value of 1.4×10^{-3} mJ in laser pulse and a power level of 0.4 MW/cm^2 with light focused through a prism onto the metal film. From the constancy of reflectance shape, size, and location, we know that there is no damage as long as the intensity remains below 1.8 MW/cm^2, corresponding to 4.5 V on the diode detector. All the data reported here were taken in the undamaged regime. At light intensities near 6 V, a damage spot is visually observed.

The maximum photoyield, defined as the ratio of emitted photoelectrons to incident photons, is near 10^{-7} electron per photon.

RESULTS

Measurements of the reflectance R and of the photoyield Y have been made on bare Ag films in vacuum, and with air or NH_3 vapor pressures from 10^{-3} to 200 Torr.

Reflectances $R(\varphi)$ display the usual ATR form[2] for both p- and s-polarized beams. As the angle is varied, the reflectance rises to a maximum where TIR occurs. At a slightly larger angle the p-polarized reflectance drops to a minimum because of coupling between the beam field and the surface-plasmon field. The dispersion relation, determined from measurements made at different photon energies, is consistent with the Fresnel relations.[2] For s-polarized light, the reflectance has a slight maximum at TIR, but no notch is observed at larger angles.

The total photoyield $Y(\varphi)$ for p polarization first gradually increases with angle after TIR and then rapidly increases to a maximum at the resonant angle φ_M which is the same as for ATR. The dispersion is the same as in SPP excitation. There is more yield at angles above resonance than below. No peak is observed in $Y(\varphi)$ for s-polarized light. With intense light and NH_3 in the system, a small s-polarized photoyield is observed over the whole angular range with decreasing magnitude as φ increases. No Y is observed when the Ag film is illuminated directly.

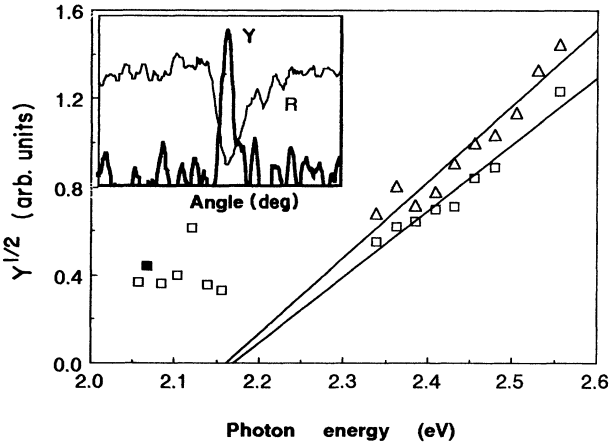

FIG. 1. Square root of peak photoyield, $[Y(\varphi_M)]^{1/2}$, as a function of p-polarized photon energy for two samples at pressures near 10^{-4} Torr of NH_3. All data were taken with the same photon flux. The lines drawn through the data indicate an apparent threshold of 2.17 eV, though there is a persistent small photopeak at lower energies, as may be seen in the inset. The inset shows a 10° span of data taken at 2.067 eV; there is a photopeak $Y(\varphi_M)$, well above noise at the same angle as the SPP minimum in the reflectance R at an incident angle near 45°. The vertical scale for the inset can be determined from the solid square in the main figure.

The magnitude of $Y(\varphi_M)$ depends on the laser intensity (see below), but also depends on photon energy at fixed laser intensity, see Fig. 1. If one looks only at the data above 2.2 eV, then a threshold near 2.2 eV is indicated, close to half the usual value, 4.3 eV. That observation is consistent with our assertion below that we are seeing photoelectrons generated by SHG photons. Yet there is a persistence of some yield at lower energies, as may be seen in the inset of Fig. 1. There, at only 2.064 eV, is clear evidence of a small yield at φ_M. We are unable to examine the intensity dependence at these low yields. The spread below the nominal threshold is much too large to be thermal or patch effects.[9] Watanabe and Gerischer[10] have explained a similar tail in water solutions as derived from surface oxide films.

High intensity alters the shape of the $Y(\varphi)$ curve; a broad shoulder emerges at angles above φ_M. At an intensity of 4.5 V, a photoyield is observed clearly over the whole angular range.

In order to determine which photoelectric processes are involved, the photoyield of the main peak is plotted as a function of light intensity in Fig. 2. The data are shown on a log-log graph, so that a quadratic dependence can be easily contrasted with other power laws. While the trends are hardly perfect, there is no chance for any power law significantly different from 2 to be applied. A square-law relationship between $Y(\varphi_M)$ and intensity is consistent with SHG though it does not distinguish between a one-photon photoelectric effect by second-harmonic generation or a true two-photon photoelectric effect.[7] The photoelectric processes away from the main

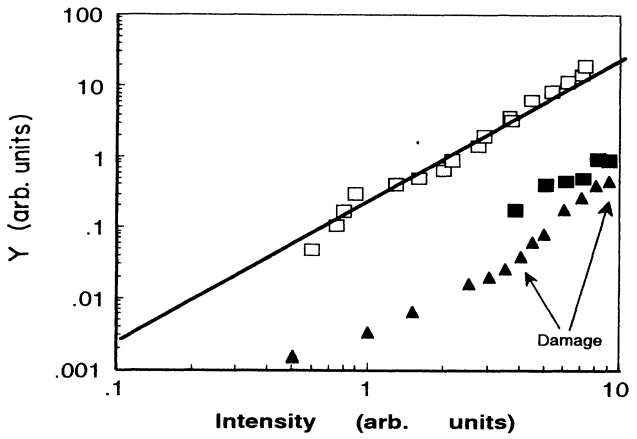

FIG. 2. Peak photoyields for several different intensities for three samples; the samples have different NH_3 partial pressures, therefore different coverages and different yields. The line shows a square-law relation. One sample was damaged at high intensities and the dependence on intensity was altered.

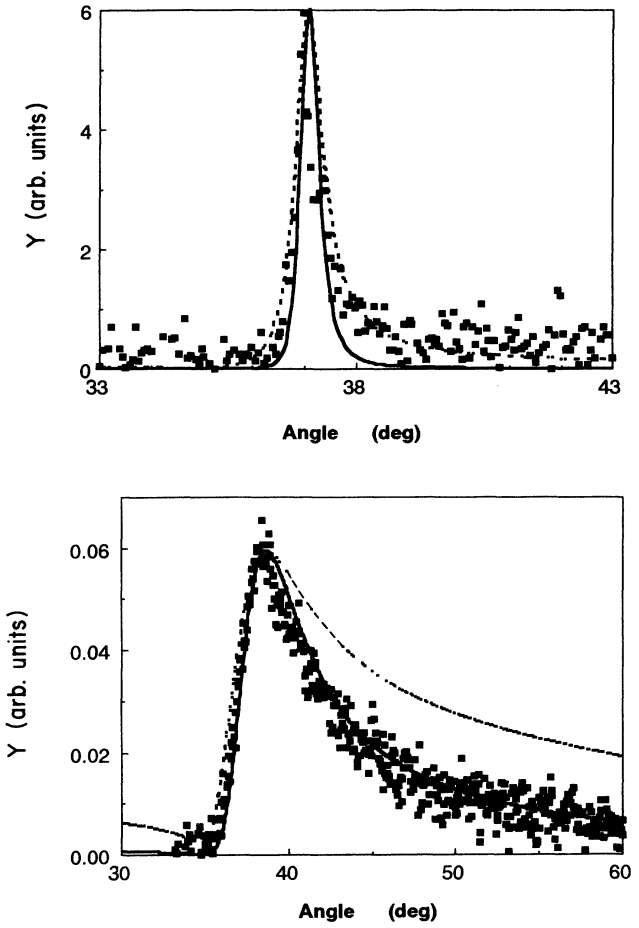

FIG. 3. Comparison of calculated and observed photoyields. The dotted lines are from Pepper's model (Ref. 11), the solid lines from the squared version of Pepper's model (see text), and the data, at 2.505 eV, are shown by solid squares. Parameters for the calculation were taken from fits to ATR data taken simultaneously. (a) Data taken on a sample ~500 Å thick. (b) Data taken on a sample only 150 Å thick.

peak depend on the gas pressure: they change from second or third order to fourth order below resonance and from third to fourth order above resonance as the gas pressure increases. At low gas pressure, different growth rates in the wings are observed. At higher gas pressure the wings have higher order.

Pepper[11] has provided a linear theory of photoemission in the ATR geometry. He computes the energy deposited at a given depth from the Poynting vector and integrates over the escape length. The theory provides a satisfactory description of normal, linear photoemission in ATR experiments above threshold.[3,5] We have adapted the model for the present, nonlinear, case by the simple expedient of squaring the energy term and integrating the escape length in the usual way. The model necessarily gives the proper angle for photoemission. We have obtained the dielectric constant and film thickness required for the photoemission calculation from fitting ATR data for the same films. The height of the yield curve is adjusted to agree with the observations, and an escape length of 50 Å is used.[12] Examples of calculated and observed photoemission are shown in Fig. 3 for two different Ag film thicknesses. A linear version of the calculation is also shown for comparison. The squared version provides a clearly better representation of the broad yield curve of the thin film; the difference is less clear for the thick film.

DISCUSSION

We have observed photoemission produced by photons with energies well below threshold. The photoemission is clearly associated with SPP excitation. Our principal evidence for SHG is the square-law relation between peak photoyield and laser intensity. In addition, there is the fact that photoemission is observed at energies well below the threshold of even adsorbate-covered Ag. Secondary support comes from the agreement found between the classical optics model for nonlinear photoyield and the observed angular dependence of the photoyield.

SHG in Ag at these energies (1.8–2.6 eV) is different from Al (Ref. 4) and from Ag at lower photon energies,[6] as second-harmonic photons (3.6–5.2 eV) are too energetic for excitation of SPP. Our samples are prepared similarly to the smooth films of Stuckless and Moskovits,[7] and therefore are inefficient two-photon sources by their standards. Thus an adsorbate is required to bring the yield up to our detection limit. NH_3 possibly creates an effective surface roughness that enhances SPP generation.

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[1]A. Otto, Z. Phys. **216**, 398 (1968).
[2]H. Raether, *Surface Plasmons on Smooth and Rough Surfaces and On Gratings* (Springer-Verlag, Berlin, 1988).
[3]T. A. Callcott and E. T. Arakawa, Phys. Rev. B **11**, 2750 (1975).
[4]H. W. Rudolf and W. Steinmann, Phys. Lett. **61A**, 471 (1977).
[5]G. Hincelin, Phys. Rev. B **24**, 787 (1981).
[6]J. C. Quail and H. J. Simon, Phys. Rev. B **31**, 4900 (1985).
[7]J. T. Stuckless and M. Moskovits, Phys. Rev. B **40**, 9997 (1989).
[8]G. T. Bennett, R. B. Coffman, and J. C. Thompson, J. Chem. Phys. **87**, 7242 (1987).
[9]*Photoemission in Solids I*, edited by M. Cardona and L. Ley, (Springer, Berlin, 1978).
[10]T. Watanabe and H. Gerischer, J. Electroanal. Chem. **122**, 73 (1981).
[11]S. V. Pepper, J. Opt. Soc. Am. **60**, 805 (1970).
[12]G. Chabrier, J. P. Goudonnet, and P. J. Vernier, Phys. Rev. B **13**, 4396 (1976).