Surface-Plasmon Cross Coupling in Molecular Fluorescence near a Corrugated Thin Metal Film

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Surface plasmons on opposite sides of a thin metal film can cross couple in the presence of a surface corrugation, or grating. We report the observation of this cross-coupling phenomenon as a radiative-decay mechanism for molecules near a corrugated thin metal film.

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A molecule placed in close proximity to a metal-dielectric interface can exhibit optical properties that are interesting and often unexpected. The early experiments of Drexhage illustrated this in a striking fashion by showing that the fluorescent lifetime of a molecule is a strong function of the separation between the molecule and a conducting surface.[1] Chance, Prock, and Silbey found excellent agreement between Drexhage's data and the predictions of a simple model in which the molecular dipole is driven by its own field reflected from the surface.[2] Their theory showed that the surface-plasmon mode of the metal-dielectric interface plays an important role in the molecule-surface interaction and they predicted that the lifetime variation should be accompanied by a separation-dependent shift in the resonance frequency of the molecule.[3] Weber and Eagen,[4] Pockrand and Brillante,[5] and others[6] observed the direct excitation of surface plasmons by decaying molecules and Holland and Hall[7] observed the predicted resonance frequency shifts by use of a system in which the molecular dipoles were replaced by small metal particles that support localized plasma resonances. The discovery of surface-enhanced Raman scattering focused widespread attention on the ability of the molecule-surface interaction to amplify the strength of a number of optical effects.[8]

We report in this Letter the observation of a radiative-decay scheme for molecules near a corrugated thin metal film that involves the cross coupling of two surface plasmons. As is well known, a thin metal film supports two surface-plasmon excitations, one associated with each of the sample's two surfaces. For an asymmetric geometry in which each surface borders a different dielectric medium, there are, then, two distinct branches of the surface-plasmon (SP) dispersion relation. It is possible to phase match, and hence couple, these two excitations by means of a grating of period Λ so that, in first order, the grating constant $k_g = 2\pi/\Lambda$ equals the difference between the propagation constants of the two modes for some frequency ω. The decay process we observe is one in which molecules decay by exciting one of the two surface plasmons which in turn excites, via the grating, the surface plasmon on the opposite interface, which then radiates by the familiar grating-coupling mechanism. Our observation of this molecular-decay process provides an unambiguous demonstration of a grating-induced cross coupling between surface plasmons on opposing surfaces of a thin film. This cross coupling was first observed by Pockrand[9] as a gap in the measured SP dispersion relation for a corrugated thin film, and was recently invoked by Brueck *et al.*[10] to explain certain reflectivity features exhibited by their Au-InP samples. Weber and Mills[11] subsequently analyzed the experimental configuration used by Brueck *et al.*[10] and argued that the reflectivity features could not have been caused by grating-induced cross coupling. We believe that our experiment is a clear demonstration of grating-induced cross coupling, and is the first to show this effect in optical emission.

Figure 1 shows both our sample and experimental geometries. Each of six glass slides was coated with a layer of Shipley photoresist which was then exposed and developed by standard holographic techniques to form shallow surface gratings. The grating periods selected were $\Lambda = 760$, 814, 898, 900, 926, and 976 nm. Each grating was then coated with a 50-nm-thick layer of high-purity silver by evaporation in a cryogenically pumped ultrahigh-vacuum system at pressures in the 10^{-8}-Torr range. The silver film replicates the grating structure to produce a corrugated metal layer bounded on one side by photoresist (refractive index $n \simeq 1.6$) and on the other side by air.

In the absence of both the corrugation and the Ag overlayer, the Shipley photoresist used in this investigation exhibits a broad fluorescence spectrum when illuminated by an appropriate laser line. This spectrum is shown in Fig. 2 as the uppermost curve that peaks near the wavelength $\lambda = 640$ nm for excitation wavelength $\lambda = 488$ nm. This same spectrum is obtained when it is measured through an uncorrugated overlayer of Ag. In our experiments with corrugated samples, the laser output at $\lambda = 488$ nm from an argon-ion laser was focused into one end of an optical fiber, the other end of which was attached to a rotation stage on which a sample was placed; see Fig. 1. The light emerging from the fiber was then collimated and

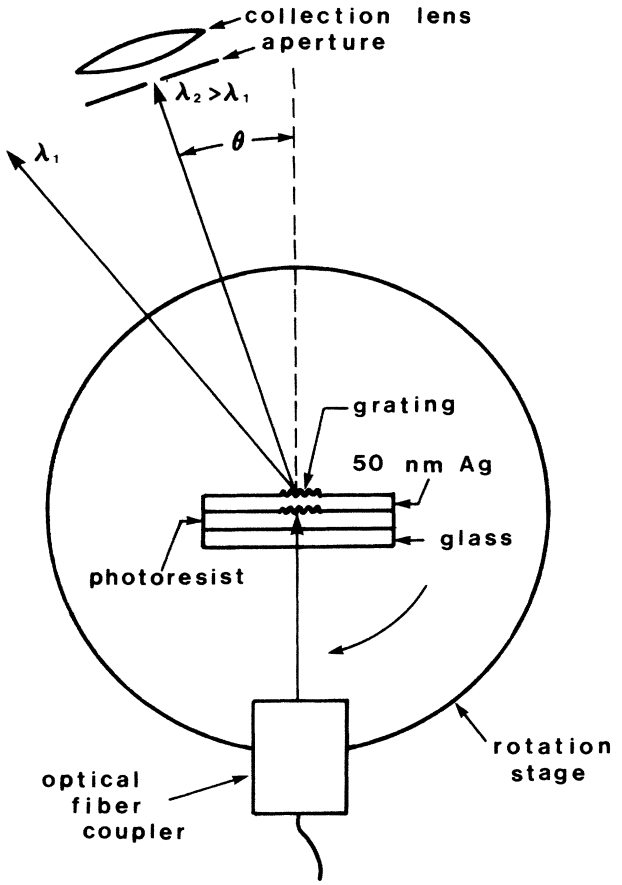

FIG. 1. Sample and experimental geometries.

directed at normal incidence onto the sample through the glass substrate. The rotation stage assembly was placed in front of the collection optics for a SPEX 1401 double monochromator followed by a photomultiplier tube and a PAR photon-counting detection system. A rectangular aperture placed in front of the collection lens limited the angular acceptance to about 2°.

Excited molecules within the photoresist can readily excite SP at the Ag-photoresist interface by both grating coupling and near-field coupling.[4-6] We measure, in our experiment, the light emitted by SP associated with the Ag-air interface. These Ag-air SP interact with the grating to radiate light of wavelength λ into a direction θ, relative the grating normal, defined by the relation

$$k_{sp} - 2\pi/\Lambda = (2\pi/\lambda)\sin\theta, \tag{1}$$

where

$$k_{sp} = (2\pi/\lambda)[\epsilon_m/(\epsilon_m + 1)]^{1/2} \tag{2}$$

is the SP propagation constant, Λ is the grating period, and ϵ_m is the relative permittivity of the metal (Ag). Equations (1) and (2) assign a very definite signature to the radiation from Ag-air SP. Because the intrinsic luminescence spectrum of the photoresist is very broad, the coupling mentioned above excites an equally broad spectrum of SP at the Ag-photoresist interface. However, for a given grating period Λ, cross coupling between the two surface plasmons can only occur, in first order, for wavelengths that satisfy

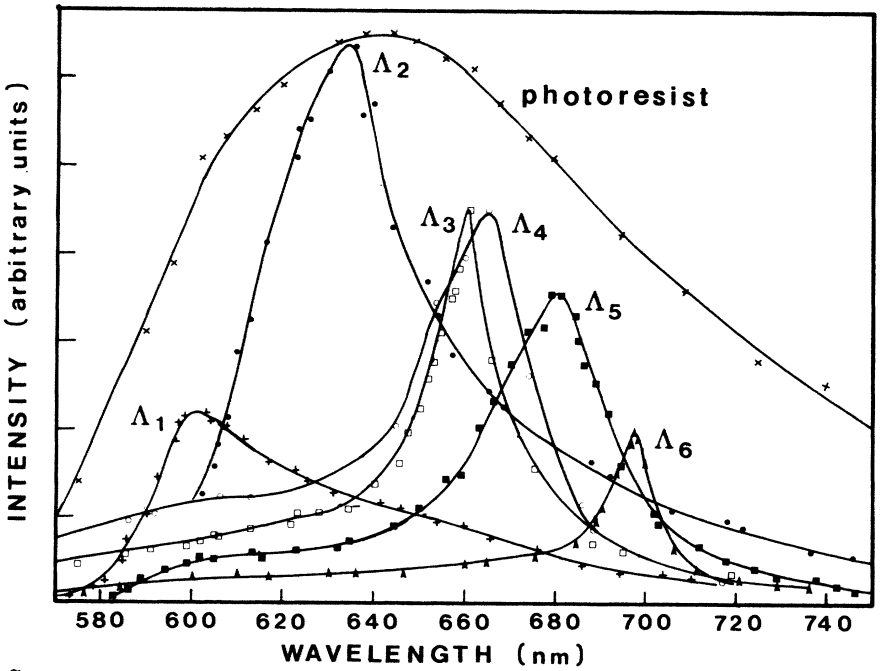

FIG. 2. Photoresist fluorescence spectrum and Ag-air interface SP radiative emission spectra for gratings having periods (in nanometers) $\Lambda_1 = 760$, $\Lambda_2 = 814$, $\Lambda_3 = 898$, $\Lambda_4 = 900$, $\Lambda_5 = 926$, $\Lambda_6 = 976$.

$\Delta k_{sp} = 2\pi/\Lambda$, where Δk_{sp} is the difference, for given λ, between the propagation constants of the SP associated with the two interfaces. Therefore only a portion of the initially excited SP spectrum at the Ag-photoresist boundary will excite SP on the Ag-air boundary.

We have measured the Ag-air SP radiation spectrum for each of our six samples by measuring the intensity of the wavelength components emitted into their corresponding angles as determined by Eqs. (1) and (2). The data are presented for all six samples in Fig. 2, beneath the curve that defines the intrinsic photoresist luminescence spectrum which defines the initial Ag-photoresist SP excitation spectrum. These curves have all been corrected for the wavelength dependence of the response of the optical system and detector. It is clear that the Ag-air SP radiation is most pronounced near a certain wavelength λ_i for the ith sample, and that λ_i changes from sample to sample as the grating period (Λ_i) changes. We attribute this phenomenon to cross coupling between the surface plasmons on the two sample surfaces: the wavelength λ_i is, in fact, the one defined by the condition $\Delta k_{sp} = 2\pi/\Lambda_i$, where Λ_i is the period of the ith grating.

To show that our interpretation is the correct one, we measured the dispersion relation for both SP modes and obtained experimental values for the quantity Δk_{sp}. For the Ag-air SP, this was accomplished during the course of the measurements that gave rise to Fig. 2. For the Ag-photoresist SP, this was accomplished by contacting a prism to the bottom of the glass substrate, illuminating the photoresist through the metalized grating from above, and measuring the angle of the resulting Ag-photoresist SP radiation as a function of wavelength. Figure 3 shows the results of these measurements for the spectral range of interest. Cross coupling at $\lambda_1 = 600$ nm for the grating with period Λ_1 is also indicated by virtue of the grating constant $2\pi/\Lambda_1$ shown connecting the two dispersion curves near λ_1, i.e., phase-matching surface plasmons on opposite sides of the metal grating. It should be noted that the density of data points in Fig. 3 is insufficient to reveal the small splitting in these curves caused by the periodic grating and reported by previous authors.[9,12,13] Figure 4 shows measured values of Δk_{sp}, at the peak emission wavelength for each grating, versus the corresponding grating constant $2\pi/\Lambda_i$. All six points $(\Delta k_{sp}, 2\pi/\Lambda_i)$ lie within a 2% error of the theoretical line given by $2\pi/\Lambda = \Delta k_{sp}$. This agreement is excellent and supports our conclusion that the emission peaks which occur in Fig. 2 are indeed caused by surface-plasmon cross coupling.

It deserves mention that the cross-coupling condition $\Delta k_{sp} = 2\pi/\Lambda$ defines a single wavelength λ_i, whereas the data in Fig. 2 show that a narrow band of wavelengths centered around λ_i actually seems to participate in the cross coupling. There are at least two factors that contribute to the broadening evident in Fig. 2. First, $\mathrm{Im}(\epsilon_m) \neq 0$ in Ag, which means that the SP resonances are broadened. Second, the collection lens samples a range of angles, and hence a broadened range of wavelengths.

Our demonstration of surface-plasmon cross coupling as a decay scheme for molecules near a corrugated metal film made use of the, in this case, fortuitous fluorescence features of Shipley photoresist. The basic process, however, is important for investigations of

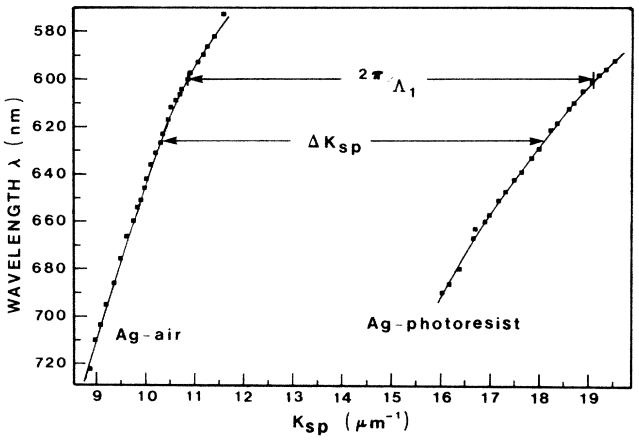

FIG. 3. Experimental dispersion curves for surface plasmons at the Ag-air and Ag-photoresist corrugated interfaces with $\Lambda_1 = 760$ nm. The grating constant $2\pi/\Lambda_1$ phase matches the two SP at $\lambda_1 = 600$ nm, the peak emission wavelength for the grating having period Λ_1.

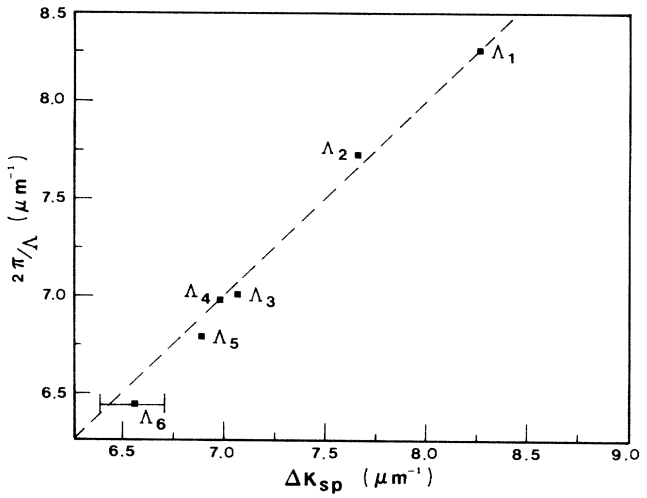

FIG. 4. Comparison of grating constant $2\pi/\Lambda_i$ with the difference Δk_{sp} between surface plasmons on opposite sides of grating Λ_i and at the same peak emission wavelength λ_i. Horizontal error bars associated with grating Λ_6 represent an estimated $\pm 3\%$ error in the measured values of Δk_{sp} and are the same size for all six points.

molecular fluorescence from molecules of any sort placed in close proximity to a corrugated metal film. The results in this paper may also be important for investigations of light emission from metal-oxide-metal tunnel junctions.[14] These structures emit light when a tunneling electron deposits its energy into one or more of the surface-plasmon–like electromagnetic modes the structure supports. A recent Letter by Ushioda, Rutledge, and Pierce[15] suggested that the optical emission from their samples occurs when a tunneling electron excites the so-called "slow" mode of the tunnel junction, which in turn cross couples to excite one of the structure's fast modes, which in turn radiates. Their samples were not intentionally corrugated, but they suggest that microscopic surface roughness might mediate the cross coupling. No such cross coupling has ever been observed directly, however; it would be quite difficult, in fact, as it would require gratings with very short periods (~ 10 nm) to phase match the two modes. While our geometry differs significantly from that of a tunnel junction, our experimental results do show that cross coupling does indeed occur as a route to optical emission in the presence of proper phase matching.

In summary, we have observed grating-induced surface-plasmon cross coupling in the decay of molecules near a corrugated thin metal film. We have shown that the cross coupling occurs under conditions in which the phase-matching condition $\Delta k_{sp} = 2\pi/\Lambda$ is satisfied. This process is an important radiative-transfer mechanism for molecules near the surface of a thin metal film. Its observation in optical emission provides direct evidence that cross coupling can occur in realistic geometries, a conclusion that could influence future consideration of the mechanisms at work in metal-oxide-metal tunnel junctions.

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