Enhanced Dipole-Dipole Interaction between Elementary Radiators Near a Surface

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We report the results of elastic light-scattering measurements of random silver nanoparticle arrays fabricated onto structures supporting optical surface modes (i.e., surface plasmons or waveguide modes). We observe dramatic, qualitative changes in the resonance structure of the nanoparticle layer due to coupling with the propagating modes. The effect appears to arise because the underlying surface modes mediate an enhanced dipole-dipole interaction between individual nanoparticles. A calculation that supports this interpretation is described. [S0031-9007(98)06415-1]

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The presence of a nearby surface or structure modifies the radiative properties of an oscillating dipole. Drexhage's elegant experiments [1] demonstrated, at optical frequencies, that for a molecular dipole placed a distance d from a metal surface (i.e., a mirror) the dipole-surface interaction causes a d-dependent variation in the molecule's radiative lifetime. This effect can be understood as resulting either from an interaction between the dipole and its own image field [2,3], or equivalently from the surface-induced modification of the density of states of the radiation field in the immediate vicinity of the dipole. Careful analysis of Drexhage's measurements identified as an important mechanism the energy transfer between the oscillating dipole and the surface plasmon (SP) mode propagating along the surface of the metal [4,5]. A single elementary radiator will strongly excite a SP or other propagating surface mode if it falls within range of the mode's evanescent field. But an additional qualitative effect should occur for a (random or ordered) two-dimensional (2D) array of dipoles that falls within that evanescent field. Under the right conditions, the propagating mode of the underlying surface will transmit energy between pairs of dipoles in the overlayer, thus modifying the dipole-dipole interaction [6]. This novel mechanism might be expected to produce, for a variety of experimental systems, effects distinctly different from, and potentially more pronounced than, those commonly associated with the dipole-surface interaction.

In an assembly of oscillating dipoles, the interaction between dipoles proceeds as $1/r^3$ for small r and as $1/r$ for large r, where r is the separation between dipoles. But for a 2D dipole array in close proximity to a suitable surface, the interaction between dipoles can proceed via a surface mode as $e^{-\alpha r}/\sqrt{r}$, where α depends on the propagation length of that mode. For a sufficiently long-lived surface mode, the range of this interaction will be large enough to couple strongly a large number of dipoles within the array. In this Letter, we report the observation of rather dramatic, qualitative changes in the optical resonance behavior of a random array of oscillators coupled as described above by the surface modes of an underlying structure. In particular, we used as a test system the optical resonances present in a layer of silver (Ag) nanoparticles, and observed how these resonances are affected by being placed near two kinds of structures: (1) single layers of metal and (2) silicon-on-insulator (SOI) wafers. The former support propagating SP modes, as mentioned above. The latter are nonmetals, each supporting a specified number of well-defined optical modes. We probe the resonance behavior of these systems through elastic light-scattering measurements. Instead of the slightly shifted spectra one might expect from the effect of a flat mirror on a nearby dipole [7], we observe scattering spectra that are qualitatively different than those for an isolated layer of nanoparticles. We attribute these changes to the surface-mode-modified dipole-dipole interaction. The predictions of a simple physical model support our interpretation.

The nanoparticle layers used in our experiments were formed by thermal deposition, under high vacuum ($<10^{-6}$ Torr), of a thin layer of silver (15–18 nm) onto each of the described samples. The samples were removed from vacuum and annealed under flowing nitrogen (or, in the case of the island/Ag-mirror geometry, a mixture of 90% nitrogen and 10% hydrogen) for 20–60 min at 185–225 °C. The annealing step causes the metal layer to form into a random array of distinct particles, referred to as a metal-island film. The fabrication conditions were adjusted to achieve an average particle diameter of ~100 nm (as determined by scanning electron microscopy), with an interparticle separation distance comparable to the particle diameters. The sub-wavelength-size particles support optical resonances arising from the excitation of localized conduction-electron plasma oscillations [8,9]. Figure 1 shows a transmission spectrum of a typical Ag island film formed on a glass slide that was first coated with a 30 nm thick lithium fluoride (LiF) layer (also formed by thermal deposition). The island resonance appears as a dip in the transmission spectrum at the resonance wavelength ($\lambda = 430$ nm), a dip resulting from *two* distinct processes within each metal particle: absorption and radiative scattering. For $\lambda > 430$ nm, the

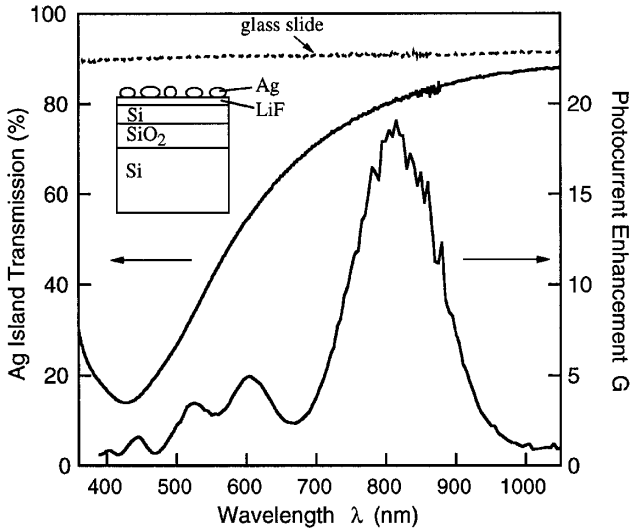

FIG. 1. Transmission spectrum of a Ag-island film on a LiF-coated glass substrate, along with the measured photocurrent enhancement G produced by an identical Ag-island film formed on an SOI photodetector. The island-SOI structure is shown in the inset; the Si and SiO_2 layer thicknesses are 160 and 200 nm, respectively.

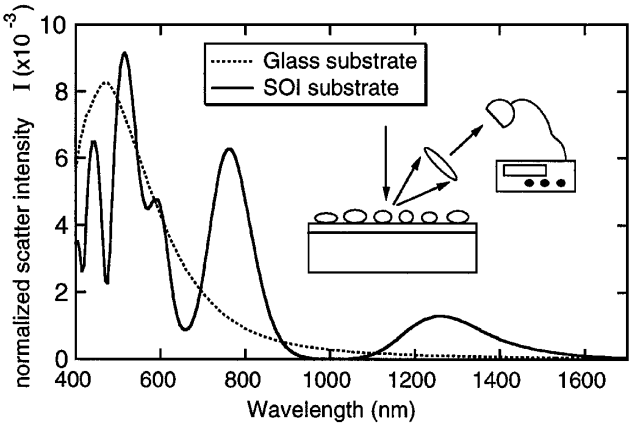

FIG. 2. The measured intensity of scattered light (normalized to the incident intensity) for a Ag-island film formed on LiF-coated glass (dotted line) and SOI (solid line). LiF thickness is 30 nm.

100 nm diameter particles are predominantly radiative [10]: Extinction in the transmission represents energy elastically scattered by the particles.

In our first set of experiments, Ag-island films were formed on commercial SOI wafers coated with LiF spacer layers of thickness d (see inset of Fig. 1). The 160 nm thick silicon (Si) layer supports three optical waveguide modes at $\lambda = 800$ nm. Light incident on this structure can excite localized plasma resonances in the particle layer, inducing polarization currents in the individual particles that radiate into the underlying structure. For d sufficiently small, the radiating nanoparticles transfer a significant portion of their energy into the SOI waveguide modes. This coupling can be observed by measuring the photocurrent generated by a photodetector fabricated directly into the thin Si layer [11]. The particle-waveguide coupling enhances absorption in the thin Si layer because the coupled light is "trapped" by the guided modes (analogous to light trapping in solar cells [12,13]). The photocurrent enhancement G produced by the Ag island layer (for $d = 30$ nm) is shown in Fig. 1. G is defined as the ratio of the detector photocurrent with/without the Ag-nanoparticle overlayer.

It is intriguing that G vs λ for the island-coupled SOI structure peaks at such a large value, $G_{\max} \sim 20$, and near $\lambda = 800$ nm, far from the $\lambda \sim 430$ nm Ag-island plasma resonance (for islands on glass). We conclude that the resonance behavior of the particle layer is being modified in an important way by interaction with the SOI waveguide modes. We investigated this effect via elastic light-scattering measurements using the geometry shown in the inset of Fig. 2. Light from a tungsten-halogen lamp passed through a monochromator to illuminate each sample at normal incidence. A detector collected diffusely scattered light over a broad angular range that excluded the specularly reflected beam ($\sim 2\pi/5$ steradians, centered at 45° off normal). We interpreted the intensity spectrum $I(\lambda)$ of the scattered light as a measure of the effective polarizability of the coupled island-waveguide system. Figure 2 shows $I(\lambda)$ for the island/SOI geometry compared to that for an identical Ag-island film on a glass substrate. In both cases, the island layer was separated from the sample surface by a 30 nm thick LiF layer. On glass, the island layer produces the expected result: A single peak near $\lambda = 470$ nm [14]. On the SOI structure, however, the spectrum is qualitatively different, consisting of strong peaks near 800 and 1300 nm, and several peaks in the 400-to-600 nm range. The peak at 1300 nm is particularly striking when compared to the island-on-glass signal, which is almost negligible at this wavelength. Measurements on samples with larger spacer thicknesses d reveal similar behavior: The number of peaks remains constant, and the peaks shift slightly to longer wavelengths as d increases. For $d \geq 170$ nm, the features at 600, 800, and 1300 nm are much weaker, consistent with the notion that the nanoparticle-mode coupling (which decreases for large d) produces the observed behavior.

We believe these strong effects occur because the presence of the waveguide significantly increases the interaction among the individual nanoparticles in a given island film. Light incident on an island film induces across each particle an electric field E that depends both on the shape of the particle and on the contributions from the neighboring particles (the dipole-dipole interaction) [15]. For films where the particles are separated by distances less than λ, the particle interactions are typically dominated by near-field effects ($E \propto 1/r^3$), although far-field effects ($E \propto 1/r$) can play a role for larger particle sizes. For islands on a waveguide, the scattered

energy is coupled into the waveguide modes, remaining localized near the island layer. The modes provide an additional mechanism for particle interaction, one which depends upon the attenuation length $L_m(\lambda)$ of the mth underlying mode ($E \propto e^{-\alpha r}/\sqrt{r}$, where α depends upon absorption and leakage in the waveguide). In each case, the largest interaction occurs for particles separated by the minimum separation distance $2r_0$ (where r_0 is the radius of the particles). It is illustrative to ask at what distance the strength of each interaction falls to 10% of maximum: For $r_0 = 50$ nm, this distance is 0.22 μm for near-field effects, 1.0 μm for far-field effects, and 4.1 μm for a particular waveguide-mediated interaction (the TE_1 [transverse electric] mode of the SOI structure at $\lambda = 760$ nm). The number of neighboring particles contributing to the induced field at any one particle can be substantially increased by the waveguide interaction. In a random array of particles, these contributions will add incoherently on average, and the size of the field induced across a single particle by the incident field (the polarizability) will increase in proportion to the number of contributing neighbor particles.

We envision the interaction proceeding in the following steps. The incident field excites plasma resonances in the nanoparticle layer, which in turn excite the mth guided mode of the SOI waveguide. The wavelength dependence of this interaction is proportional to $f_m(\lambda)\sigma(\lambda)$, where $\sigma(\lambda)$ is the measured scattering spectrum of the isolated island layer, and $f_m(\lambda)$ is the fraction of energy emitted into the mth guided mode by a single dipole located a distance d above the surface. The propagating modes couple energy back into the nanoparticle layer in a reciprocal process that can be estimated to proceed also as $f_m(\lambda)\sigma(\lambda)$. Each particle in the layer receives energy from all of its neighbors within an interaction area determined by the propagation length of the mode (area $\propto [L_m(\lambda)]^2$). A small fraction $f_{\mathrm{air}}(\lambda)$ of this energy is radiated into free space, and it is this signal we detect and record. For a simple estimate, we model the relative wavelength dependence of the total interaction via $\chi_m(\lambda)$, which we define as the product of the strengths of each of the four processes:

$$\chi_m(\lambda) = [f_m(\lambda)\sigma(\lambda)]^2 L_m^2(\lambda) f_{\mathrm{air}}(\lambda). \qquad (1)$$

$L_m(\lambda)$ can be obtained from the waveguide dispersion relation for wavelengths ($\lambda < 900$ nm) at which the mode attenuation is dominated by absorption in the waveguide material, i.e., where the output-coupling effects of the islands can be neglected. Using a procedure outlined in Ref. [16], the theory of Ref. [5] can be used to calculate both $f_m(\lambda)$ and $f_{\mathrm{air}}(\lambda)$.

Plots of χ_m for several modes of the SOI waveguide are shown in Fig. 3, along with the scattering spectrum for the nanoparticle-SOI structure from Fig. 2. The results suggest an interesting interpretation: *Each of the peaks in the observed scattering spectrum can be associated with the optimum coupling range of a particular mode of the SOI waveguide.* Indeed, there is a very good agreement between the location and width of the curves for the TE_1, TE_2, and TM_1 (transverse magnetic) modes and the corresponding features in the experimental data, although there is less agreement for the TM_2 mode. Below $\lambda = 500$ nm, the short propagation length of the modes (due to absorption in the Si layer) reduces the magnitude of the modal coupling effects, and the data in this region may be dominated by other processes. The curves for the two lowest-order modes (TE_0 and TM_0) are not shown; our assumption regarding $L_m(\lambda)$ breaks down above 900 nm. Based on our interpretation, however, we can associate the peak in our data at 1300 nm with the TM_0 mode, and expect that another peak due to the TE_0 mode exists at even longer wavelengths (beyond the range of our detection equipment). That the simple estimate in Eq. (1) succeeds reasonably well lends support for our interpretation.

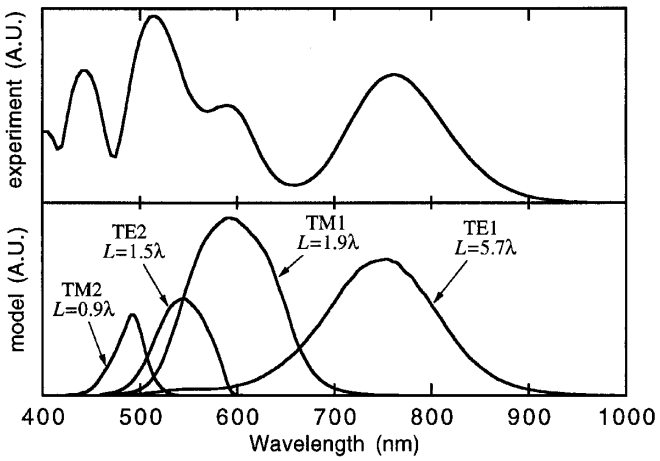

FIG. 3. Plots of χ_m for several modes of the SOI waveguide (bottom curves). Each curve is labeled with the corresponding mode and the coupling range L associated with that mode at the peak wavelength of the interaction. The scattering spectrum for the nanoparticle-SOI structure from Fig. 2 is also shown (top curve).

As a further test of our interpretation, we investigated the scattering spectra $I(\lambda)$ of Ag-island films formed on a layer of silver (200 nm thick) coated with LiF spacer layers of thickness d (see Fig. 4). For $d < 150$ nm, the silver-LiF structure supports a *single* mode (the surface plasmon), with a second mode (TE_0) appearing when d exceeds this value. For most of the wavelength range investigated, the SP attenuation length is longer than that of the SOI waveguide modes, so one expects a correspondingly stronger interaction. Indeed, for all values of d shown in Fig. 4, $I(\lambda)$ is significantly enhanced with respect to the (weaker) island-on-glass sample (top curve, expanded by 25×). For $d \leq 100$ nm, $I(\lambda)$ consists of a single broad peak, corresponding to the single mode of the underlying surface. As d is increased further,

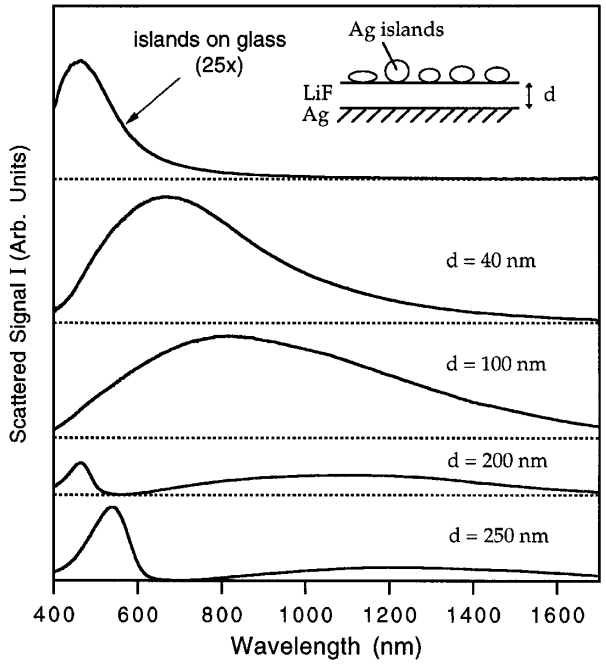

FIG. 4. The measured intensity of scattered light (normalized to the incident intensity) for the Ag-islands/LiF/Ag-mirror geometry. The Ag-islands/LiF/glass signal is shown as the top curve, expanded by 25×,

the broad peak due to the SP mode shifts to longer wavelengths and decreases (reduced coupling strength), and a second peak appears. The appearance of this second peak (due to the TE_0 mode) supports our hypothesis regarding the physical mechanism producing these results. Equation (1) can be used to make predictions for this geometry, but requires a theoretical description of $L_m(\lambda)$ in the strong island-output-coupling regime.

The size of the metal nanoparticles plays an important role in the observed effects. Larger nanoparticles have larger polarizabilities, and likewise higher radiative efficiencies; both factors increase the degree of particle interaction. Layers of smaller-sized particles lead to small absorption enhancements (G) in the SOI geometry, and also show significantly reduced scattering in this geometry at wavelengths away from the bare-island resonance. This might explain why investigators who have worked with similar geometries (island layers on mirrors) [7,17] have not reported these effects. The enhancements in absorption and elastic scattering we observe are likely associated with the existence of strongly enhanced local fields at those wavelengths. The local-field enhancements produced by metal-nanoparticle resonances are known to cause a variety of important optical effects, such as surface-enhanced Raman scattering [18] and enhanced second harmonic generation [19]. Our results indicate that these enhancements can be made to occur over a wide range of wavelengths, making these structures potentially useful for enhancing multifrequency nonlinear interactions to a degree exceeding previous observations. Further investigations will be necessary to determine the full potential of these structures.

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[1] K. H. Drexhage, in *Progress in Optics*, edited by E. Wolf (North-Holland, Amsterdam, 1974), Vol. 12, pp. 163–232.
[2] H. Morawitz, Phys. Rev. **187**, 1792–1796 (1969).
[3] H. Kuhn, J. Chem. Phys. **53**, 101–108 (1970).
[4] H. Morawitz and M. R. Philpott, Phys. Rev. B **10**, 4863–4868 (1974).
[5] R. R. Chance, A. Prock, and R. Silbey, in *Advances in Chemical Physics*, edited by I. Prigogine and S. A. Rice (Wiley, New York, 1978), Vol. 37, pp. 1–65.
[6] M. R. Philpott, J. Chem. Phys. **62**, 1812–1817 (1975).
[7] W. R. Holland and D. G. Hall, Phys. Rev. Lett. **52**, 1041–1044 (1984).
[8] R. R. Singer, A. Leitner, and F. R. Aussenegg, J. Opt. Soc. Am. B **12**, 220–228 (1995), and references therein.
[9] P. Rouard and A. Meesen, in *Progress in Optics*, edited by E. Wolf (North-Holland, Amsterdam, 1977) Vol. **15**, pp. 77–137, and references therein.
[10] J. Gersten and A. Nitzan, J. Chem. Phys. **75**, 1139–1152 (1981).
[11] H. R. Stuart and D. G. Hall, Appl. Phys. Lett. **69**, 2327–2329 (1996).
[12] E. Yablonovitch and G. D. Cody, IEEE Trans. Electron Devices **29**, 300–305 (1982).
[13] The nanoparticle layer also acts as an efficient output-coupling mechanism, and there exists an upper limit to the achievable absorption imposed by the second law of thermodynamics. See H. R. Stuart and D. G. Hall, J. Opt. Soc. Am. A **14**, 3001–3008 (1997).
[14] The absorption and scattering cross sections differ slightly in their dependence on the polarizability of the island film, and this results in a small difference in the resonance wavelength for the two measurements.
[15] M. Meier, A. Wokaun, and P. F. Liao, J. Opt. Soc. Am. B **2**, 931–949 (1985).
[16] G. W. Ford and W. H. Weber, Phys. Rep. **113**, 195–287 (1984).
[17] A. Leitner *et al.*, Appl. Opt. **32**, 102–210 (1993).
[18] M. Moskovits, Rev. Mod. Phys. **57**, 783–826 (1985).
[19] A. Wokaun *et al.*, Phys. Rev. B **24**, 849–856 (1981).