Enhanced Raman scattering from self-affine thin films

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Surface-enhanced Raman scattering (SERS) from a self-affine surface is shown to be very large. A theory is developed expressing this SERS in terms of the eigenmodes of a self-affine surface; the theory successfully explains the observed SERS from cold-deposited thin films that are known to have a self-affine structure. Spatial distributions of local fields at the fundamental and Stokes frequencies are strongly inhomogeneous and contain hot zones (high-field areas) localized in nanometer-sized regions that can be spatially separated for the two waves. © 1996 Optical Society of America

Surface-enhanced Raman scattering (SERS) from rough thin films is commonly associated with excitation of surface plasmon oscillations.[1] Rough thin films, formed when an atomic beam condenses onto a low-temperature substrate, are typically self-affine fractal structures.[2] In contrast to the case of usual roughness, there is no correlation length for self-affine surfaces, which implies that inhomogeneities of all sizes are present (within a certain size interval) according to a power-law distribution. [To reveal the scale invariance, a self-affine surface requires different scaling factors in the (x, y) plane and in the normal (growth) direction, z.[3]] The existing theories greatly simplify SERS from cold-deposited films, treating them as either a collection of particles of various shapes or a slightly modulated plane surface.[1]

On a self-affine surface, collective plasmon oscillations are strongly affected by the fractal morphology of the surface. In particular, these modes become spatially localized, leading to hot and cold spots (areas of high and low local fields); the spatial distributions of these spots are very sensitive to the frequency and polarization of the applied field.[4]

In this Letter we show that SERS on a self-affine thin film is due to resonant excitation of the eigenmodes of the film, resulting in very high local fields at the fundamental and Stokes frequencies. The hot spots at the two frequencies can be localized in spatially separated nanometer-sized regions. Near-field scanning optical microscopy,[5] with its subwavelength resolution, will permit the effects under consideration to be observed experimentally.

To simulate a self-affine surface, we used the restricted solid-on-solid (RSS) model, which generates surfaces with fractal dimension $D = 2.6$ (Ref. 6) and closely approximates cold-deposited metal (in particular, silver) films[2] [see Fig. 1(a)]; for details on simulating self-affine thin films and their linear optical properties, see Ref. 4.

To calculate optical excitations of a self-affine thin film by an incident wave, $\mathbf{E}^{(0)} \exp(-i\omega t + i\mathbf{k} \cdot \mathbf{r})$, we used the discrete dipole approximation[7] (DDA). In the DDA, one replaces an odd-shaped object by an array of N point dipoles, with the spacing between the dipoles small compared with the wavelength and with the sizes of spatial inhomogeneities. Each dipole has an oscillating polarization driven by both the incident wave and the electric fields resulting from all the dipoles in the array. Assuming that the sample size is much smaller than the wavelength λ [so that the quasi-static approximation is valid and $\exp(i\mathbf{k} \cdot \mathbf{r}) \approx 1$], we can obtain the self-consistent solutions for the dipole polarizations (oscillating at frequency ω) as the solutions to a set of the coupled-dipole equations[4,7,8] (CDE's):

$$d_{i,\alpha} = \alpha_0 \left[E_\alpha^{(0)} + \sum_j W_{ij,\alpha\beta} d_{j,\beta} \right], \qquad (1)$$

where $\mathbf{d}_i$ is the amplitude of the dipole moment induced at the ith site and $W_{ij,\alpha\beta} = -(\delta_{\alpha\beta} r_{ij}{}^2 - 3r_{ij,\alpha} r_{ij,\beta})/r_{ij}{}^5$ is the interaction operator between two dipoles, with radius vectors $\mathbf{r}_i$ and $\mathbf{r}_j$. The greek subscripts denote Cartesian components (which should not be confused with the polarizability, α). Summation over repeated greek subscripts is implied. Note that the time-dependent factor $\exp(-i\omega t)$ is canceled from both sides of Eq. (1).

For the polarizability, $\alpha_0 \equiv \alpha_0(\omega)$, of each individual dipole, the Clausius–Mossotti relation is used[4,7]: $\alpha_0 = (3/4\pi n)[(\epsilon - 1)/(\epsilon + 2)] = R_m{}^3[(\epsilon - 1)/(\epsilon + 2)]$, where $\epsilon \equiv \epsilon'(\lambda) + i\epsilon''(\lambda)$ is the bulk dielectric function and n is the number density of dipoles [for point dipoles located on a cubic lattice with the period a, $n = a^{-3}$; see Fig. 1(a)]. The latter expression for α_0 describes the polarizability of a sphere with radius $R_m = (3/4\pi)^{1/3}a$, which makes the total volume of all the spheres equal to the volume of original object under consideration.[4] Thus, in the DDA, one can equally consider point dipoles or equivalent spheres with radius R_m defined above.

At $\epsilon'(\lambda) = -2$ there is a resonance for excitation of an individual dipole (sphere). As follows from Eq. (1), the spectral dependence of the solutions occurs only through $\alpha_0(\omega)$. Therefore it is convenient to introduce the quantity $Z = \alpha_0{}^{-1} = -(X + i\delta)$, where $X \equiv -\mathrm{Re}(\alpha_0{}^{-1}) = -R_m{}^{-3}[1 + 3(\epsilon' - 1)/|\epsilon - 1|^2]$ and $\delta \equiv -\mathrm{Im}(\alpha_0{}^{-1}) = 3R_m{}^{-3}\epsilon''/|\epsilon - 1|^2$. The variable X
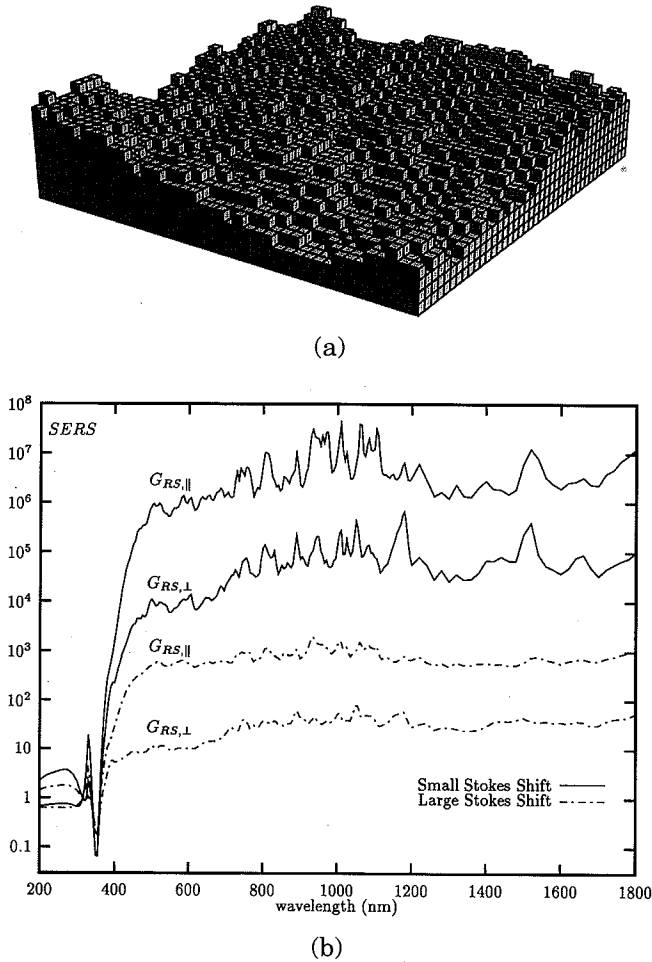
(a)

(b)

Fig. 1. (a) Self-affine film obtained in the RSS model ($D = 2.6$). (b) The enhancement of Raman scattering, $G_{RS,\parallel} = (G_{RS,x} + G_{RS,y})/2$ and $G_{RS,\perp} = G_{RS,z}$, on silver self-affine films for small and large Stokes shifts [see Eqs. (5) and (6)].

indicates the proximity to resonance of an individual particle and, thus, plays the role of a frequency parameter; δ characterizes dielectric losses. (The smaller the δ, the higher the resonance quality factor: $q \sim \delta^{-1}$.) For a specific material, using the spectral dependence $\epsilon(\lambda)$ and the above formulas, one can find the $X(\lambda)$ and $\delta(\lambda)$ dependences. (For silver, for example, these dependences are given in Refs. 4 and 8.)

By diagonalizing the interaction matrix $W_{ij,\alpha\beta}$ we can express the local fields $\mathbf{E}_i$ in terms of the eigenfunctions $\langle i\alpha|n\rangle$ and eigenvalues w_n of the operator W (Refs. 4 and 8):

$$E_{i,\alpha} = \alpha_0^{-1} d_{i,\alpha} = Z \sum_j \alpha_{ij,\alpha\beta} E_\beta^{(0)},$$

$$\alpha_{ij,\alpha\beta} \equiv \alpha_{ij,\alpha\beta}(\omega) = \sum_n \frac{\langle i\alpha|n\rangle\langle n|j\beta\rangle}{(Z - w_n)}. \quad (2)$$

The total polarizability of the ith dipole is given by $\alpha_{i,\alpha\beta} = \sum_j \alpha_{ij,\alpha\beta}$. Note that since W is a real Hermitian operator its eigenfunctions are also real.

Suppose that Raman-active molecules cover homogeneously the surface of a self-affine film, so that each site at the film–air interface, apart from the linear

polarizability $\alpha_0(\omega)$, also possesses a Raman polarizability κ, for example, as a result of Raman-active molecules absorbed on the surface of the film. Then, in addition to dipoles $\mathbf{d}_i \exp(-i\omega t)$, the applied field induces dipole moments $\mathbf{d}_i{}^s \exp(-i\omega_s t)$ oscillating with the Stokes-shifted frequency ω_s. To avoid nonessential complications, we assume that κ is a scalar. For spontaneous Raman scattering, the Raman polarizabilities κ_i at different sites contain uncorrelated phases, $\langle \kappa_i\kappa_j\rangle = |\kappa|^2\delta_{ij}$, where the angle brackets denote averaging over the ensemble of random samples (not to be confused with the bra and ket vectors), and i and j are the dipoles at the interface only.

The field acting on a Raman-active molecule at the ith site of the interface is the local field $\mathbf{E}_i$ rather than the applied field $\mathbf{E}^{(0)}$. Also, the interaction of the dipoles at the Stokes-shifted frequency ω_s should be included. As a result, the CDE's for the Stokes dipoles have the form[8]

$$d_{i,\alpha}{}^s = \kappa_i E_{i,\alpha} + \alpha_0{}^s \sum_j W_{ij,\alpha\beta} d_{j,\beta}{}^s, \quad (3)$$

where $\alpha_0{}^s = \alpha_0(\omega_s)$ is the linear polarizability at ω_s, and the local fields, $E_{i,\alpha}$, at the fundamental frequency ω are given in Eqs. (2).

The enhancement of Raman scattering, G_{RS}, is defined as $G_{RS} = \langle|\sum_i \mathbf{d}_i{}^s|^2\rangle/[N_0|\kappa|^2|E^{(0)}|^2]$, where N_0 is the number of Raman-active molecules.

Using the eigenfunctions of the interaction matrix, W, we can find solutions to the CDE's in Eq. (3) for the Stokes dipoles [similarly as for Eqs. (1) and (2)] and express the SERS enhancement in the following form:

$$G_{RS} = \frac{|Z_s Z|^2}{|E^{(0)}|^2} \left\langle \alpha_{j,\beta a}{}^s [\alpha_{j,\beta\gamma} E_\gamma^{(0)}] \alpha_{j,\delta\alpha}{}^{s*} [\alpha_{j,\delta\delta'}{}^* E_{\delta'}^{(0)*}] \right\rangle_S, \quad (4)$$

where $Z_s = Z(\omega_s) = -(X_s + i\delta_s)$ and $\alpha_i{}^s \equiv \alpha_i(\omega_s)$. The terms in the square brackets in Eq. (4) give the local fields at the fundamental frequency ω acting on the jth site. The term $\langle\ldots\rangle_s$ in Eq. (4) denotes an average over positions of dipoles on the surface of the film only.

Below, we assume that light is linearly polarized along the η axis. If the difference $\omega - \omega_s$ is small (small Stokes shift), we can put $Z_s \approx Z$ and $\alpha_j{}^s \approx \alpha_j$. Then, for the applied field polarized in the η direction, the enhancement in Eq. (4) can be expressed as

$$G_{RS,\eta} = |Z|^4 \left\langle \sum_\alpha |(\alpha_j{}^2)_{\alpha\eta}|^2 \right\rangle_S, \quad (5)$$

where $(\alpha_j{}^2)_{\alpha\beta} = \alpha_{j,\gamma\alpha}\alpha_{j,\gamma\beta}$. In the other limiting case (large Stokes shift), ω_s lies outside the band of the eigenmodes, and the interaction between the Stokes dipoles in Eq. (3) can be neglected, so that $\alpha_{i,\alpha\beta}{}^s \approx \delta_{\alpha\beta} Z_s^{-1}$. Accordingly, the enhancement in Eq. (4) acquires the form

$$G_{RS,\eta} = |Z|^2 \left\langle \sum_\alpha |\alpha_{j,\alpha\eta}|^2 \right\rangle_S. \quad (6)$$
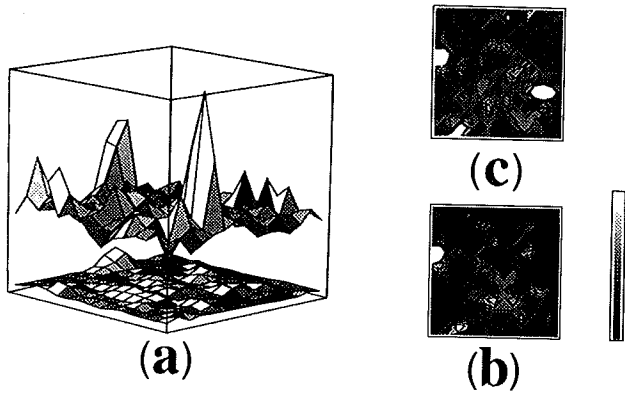
Fig. 2. (a) Spatial distributions for the local fields at the fundamental frequency, $\lambda = 550$ nm (bottom plot; the field distribution is magnified by 3), and for the Stokes fields, $\lambda_s = 600$ nm (top plot). (The applied field is linearly polarized in the plane of the Ag film.) (b), (c) The contour plots for the field distributions shown in (a).

From Eqs. (2) and (3) we also find the intensities, $I_i{}^s = I^s(\mathbf{r}_i) = |\mathbf{E}_i{}^s|^2$, of the local fields at the Stokes frequency:

$$I_i{}^s = |Z_s|^4 |\kappa|^2 \sum_\alpha \sum_{j \in S} |\alpha_{ij,\alpha\beta}{}^s E_{j,\beta}|^2, \qquad (7)$$

where the summation is over dipoles on the surface only and $\alpha_{ij,\alpha\beta}{}^s \equiv \alpha_{ij,\alpha\beta}(\omega_s)$ is given by an expression similar to Eqs. (2), with the replacement $Z \to Z_s$. Note that $I_i{}^s$ in Eq. (7) is proportional both to the local field intensity at the frequency ω and to the resonant factor associated with $\alpha_{ij}{}^s$. Thus oscillations generated at the Stokes frequency ω_s can also be in resonance with the surface eigenmodes, provided that the Stokes shift is not too large. It is important that, in general, ω_s can be in resonance with other surface modes than the incident frequency ω.

In the large-Stokes-shift case $\alpha_{ij,\alpha\beta}{}^s \approx Z_s{}^{-1} \sum_n \langle i\alpha|n\rangle\langle n|j\beta\rangle = Z_s{}^{-1}\delta_{ij}\delta_{\alpha\beta}$, and Eq. (7) is transformed into $I_i{}^s = |Z_s\kappa|^2 I_i$, where $I_i = |\mathbf{E}_i|^2$ are the local field intensities at the fundamental frequency ω. In this case, the spatial field distribution of the Raman signal at ω_s simply follows the distribution of the local fields at the frequency ω.

In Fig. 1(b) we show the average enhancement of Raman scattering for both small and large Stokes shifts on self-affine films generated in the RSS model. For the dielectric function of silver, $\epsilon(\lambda)$, we used the data of Ref. 9. The results of calculations were averaged over 12 random samples with $N \sim 10^3$ dipoles in each sample. As seen in the figure, the enhancement increases toward the long-wavelength part of the spectrum and reaches very large values, $\sim 10^7$; this agrees well with the experimental observations of SERS on cold-deposited thin films.[1] Note that the

present SERS theory is developed from first principles and contains no adjustable parameters.

In Fig. 2 the field spatial distributions at the fundamental and Stokes frequencies are shown (we chose $|Z_s\kappa|^2 = 0.25$). As seen in the figure, the distributions contain hot spots, where the fields are very high. The spatial positions of these spots are strong functions of the frequency and polarization of the applied field.[4] Although the Stokes signal is proportional to the local field at the fundamental frequency ω the generated Stokes field, with frequency ω_s, excites, in general, other eigenmodes. Hence the field spatial distributions produced by the applied field and by the Raman signal can be different, as clearly seen in the figure. [As shown in Fig. 2 for the field distributions at frequencies ω and ω_s, the spots at the left-hand sides of Figs. 2(b) and 2(c) are spatially correlated, whereas the largest Stokes peak is positioned at the right, where the ω field is relatively small.]

This picture is expected to be typical for various optical processes in strongly disordered fractal systems, such as self-affine thin films. Specifically, hot spots associated with fields at different frequencies and polarizations can be localized in spatially separated nanometer-sized areas. These novel nano-optical effects can be probed with near-field optical scanning microscopy providing subwavelength resolution.

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