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Local field distribution in random metal–dielectric films; theory and experiment

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Abstract

The local field properties of metal–dielectric films are investigated in terms of the probability distribution function (PDF). For metal coverage p, close to the percolation threshold we obtain a wide, lognormal PDF which for low metal concentrations gradually transforms into a scaling, power-law distribution function. Strong enhancement of the local fields in a broad spectral range is verified by an exact numerical procedure. In experimental studies, metal–dielectric films were synthesized by a pulsed laser deposition technique, and their optical properties were investigated using near-field optical microscopy. The experimentally and numerically obtained probability functions are found to be in good agreement.

Keywords: Semicontinuous films; Local-field distribution; Metal–dielectric film

The discovery of surface-enhanced nonlinear optical processes such as Raman and hyper-Raman scattering has brought a lot of attention to the physics of nonlinear optics [1]. Randomly roughened metal surfaces and fractal aggregates composed of nanometer size particles exhibit strong local field enhancement when illuminated by an electromagnetic wave. The local field is localized in small spatial areas, "hot" spots and results from surface plasmon resonance [2–5]. It was numerically and analytically predicted that the average Raman enhancement of the local field in silver semi continuous films and fractal aggregates is on the order of 10^6 and can be even higher in the near-infrared spectral range [3]. This broadband enhancement is due to the variety of cluster lengths that exist for metal concentrations close to the percolation threshold value $p_c = 0.5$.

In the limit of small particles sizes $\alpha \ll \lambda$ (λ is the wavelength of the incident beam) one can introduce local potential $\varphi(\mathbf{r})$ and local electric field $\boldsymbol{E} = -\nabla\varphi(\mathbf{r})$. In order to find the spatial distribution of the electric field in the quasi-static approximation we write the current conservation law, $\nabla[\sigma(\mathbf{r})(-\nabla\varphi(\mathbf{r}) + \boldsymbol{E_0}] = 0]$, where $\boldsymbol{E_0}$ is the incident electric field. The spatially dependent conductivity $\sigma(\mathbf{r})$ takes alternative values of σ_d, for the dielectric voids and σ_m, for the metal particles. To solve the current conservation law we discretize the differential equation over a square lattice, where each site is connected to the neighboring sites through four bonds. Under the

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above consideration, the problem of obtaining the local field is reduced to the solution of system of Kirchhoff's equations. Written in a matrix form it is given by the equation $\hat{H}\boldsymbol{W} = \boldsymbol{F}$, where the Kirchhoff's Hamiltonian (HK) $\hat{H}$, is a symmetrical matrix with diagonal and off diagonal elements and the current $\boldsymbol{F}$ depends on the incident field. To find the site potentials $\boldsymbol{W} = \{\varphi\}$ exactly we apply the Block Elimination (BE) procedure [6], where we impose a periodical boundary condition. Under this condition, the matrix HK has rank $L^4 - 1$, (L is the lattice size) and is incomplete. In order to make the system complete we need to ground one of the corners potential, for example $\varphi(1,1) = 0$. The Block Elimination can solve Kirchhoff's equations in L^4 single operations (to be compared with L^6 operations needed for the Gaussian elimination procedure) thus making it possible to investigate large systems comprising up to one million metal particles.

Random metal–dielectric composites represent the simplest type of disordered media. They can be produced by random deposition of metal particles on an insulating surface and statistically are described by a variety of critical exponents [7]. We model a percolation film by assigning to each bond, conductivity $\sigma_s = -i\omega\varepsilon_s/4\pi$; where we pick for ε_s the value of ε_m, with probability p, and alternatively the value of ε_d, with probability $1 - p$. For the metal permittivity we use the Drude approximation; $\varepsilon_m = \varepsilon_b - (\omega_p/\omega)^2/(1 + i\omega_\tau/\omega)$, where ε_b is contribution due to inter-band transitions, ω_p is the plasma frequency, and $\omega_\tau = 1/\tau \ll \omega_p$ is the relaxation rate. For silver we have $\varepsilon_b = 5.0, \omega_p = 9.1\,\text{eV}$, and $\omega_\tau = 0.021\,\text{eV}$ [8]; for the glass substrate, we used $\varepsilon_d = 2.2$. We sampled the probability distribution function (PDF) in terms of $\log_{10} I$, where $I = (|\boldsymbol{E}|/|\boldsymbol{E_0}|)^2$ is the local field intensity with $|\boldsymbol{E_0}|^2$ the intensity of the applied field. The logarithmic sampling was chosen in order to capture most of the relevant features that are present in the wide probability functions. In Fig. 1 we have plotted the PDF for three different metal filling factors: $p = 0.5$, 0.01 and 0.001. For the incident field we pick wavelength $\lambda = 370\,\text{nm}$, which corresponds to the single-particle plasmon resonance given by the condition $\varepsilon_d = -\text{Re}(\varepsilon_m)$. We have also calculated the case when there is only one metal bond (dipole) in the center of the film. It is important to note that the local field distribution

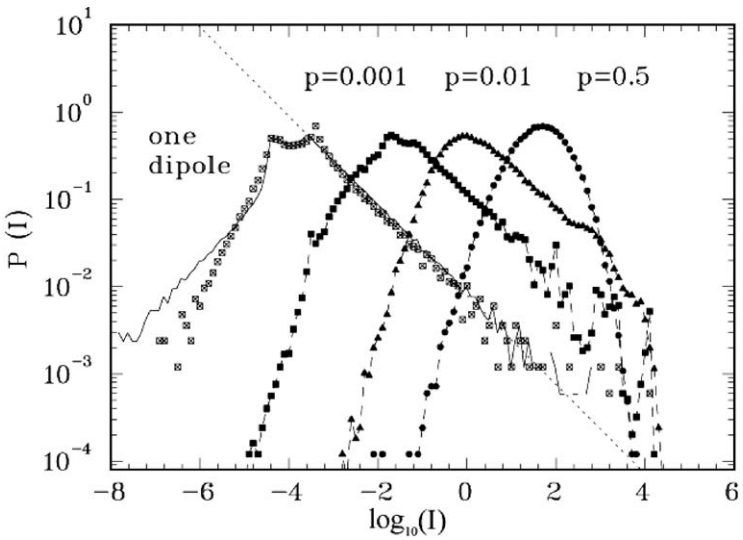

Fig. 1. Local-field distributions, $P(I)$ for silver-glass films calculated for three different metal filling factors p. The lognormal distribution for $p = 0.5$ gradually transforms into a single dipole distribution; the dotted line represents the analytical solution $P_{dip}(I)$.

is non-Gaussian and for $p = p_c$ has a form close to the lognormal function:

$$P(I) = \frac{1}{I\sigma\sqrt{2\pi}} \exp\left(-\frac{(\log_{10} I - \langle \log_{10} I \rangle)^2}{2\sigma^2}\right), \quad (1)$$

where $\langle \log_{10} I \rangle$ is the average value for the logarithm of the local field intensity I and σ is the standard deviation in terms of $\langle \log_{10} I \rangle$. This approximation seems to work sufficiently well around the average value $s = \langle \log_{10} I \rangle$. We note, however, that according to Ref. [9], where the current distribution was studied, Eq. (1) probably fails for the intensities I far from the logarithmic average s. By introducing a new substitution method, Zekri et al. [10] obtained distributions similar in shape to PDF shown in Fig. 1. However, those distributions were shifted significantly toward smaller values of I, which lead the authors to the conclusion that there is no strong enhancement of the local field. Such a conclusion contradicts the earlier calculations [2–4], experimental observations [5], and the current simulations based on the exact BE method. All these simulations and experiments indicate the existence of a large local-field enhancement in percolation metal–dielectric films that is due to the plasmon resonance. In Fig. 1 we can also see that with the decrease of the metal concentration there is an apparent transition from the lognormal distribution (for $p = p_c$) into a power-law distribution. This can be explained by the fact that with the increase of the average distances between the metal particles, their interactions become negligible and we can view the sample as a system that is separate, non-interactive, induced from the external field dipoles. For the 2D system, the intensity of the dipole field falls as $I_{dip} = 1/r^4$ and we can directly obtain the PDF by solving the integral $P(I) = \int \delta(I - I_{dip}(r))\,dS$, where d is the Dirac delta-function and S represents the surface of the integration. We find a relation $P(I) \sim I^{-3/2}$ which perfectly fits the scaling region that appears in our numerical calculations. Such universal scaling was also obtained for fractals [11], where the scaling index 'a' was found to be close to 1.5 and explained by the vector nature of the dipole fields.

The local field distribution was also obtained experimentally by using near field scanning optical microscopy (NSOM) performed on semicontinuous films [12]. The metal–dielectric films were synthesized by laser ablation of a solid silver target onto a glass surface. The local optical signal was collected by a tapered, uncoated optical fiber with a tip radius of about 50 nm. Tip-sample separation during NSOM experiments was maintained at a distance of $h \sim 10$ nm by non-optical shear-force feedback. In Fig. 2 we compare the averaged over NSOM resolution limit numerical calculations for two wavelengths $\lambda = 543$ nm and $\lambda = 633$ nm with the experimentally obtained distributions. We see good agreement between the experiment and

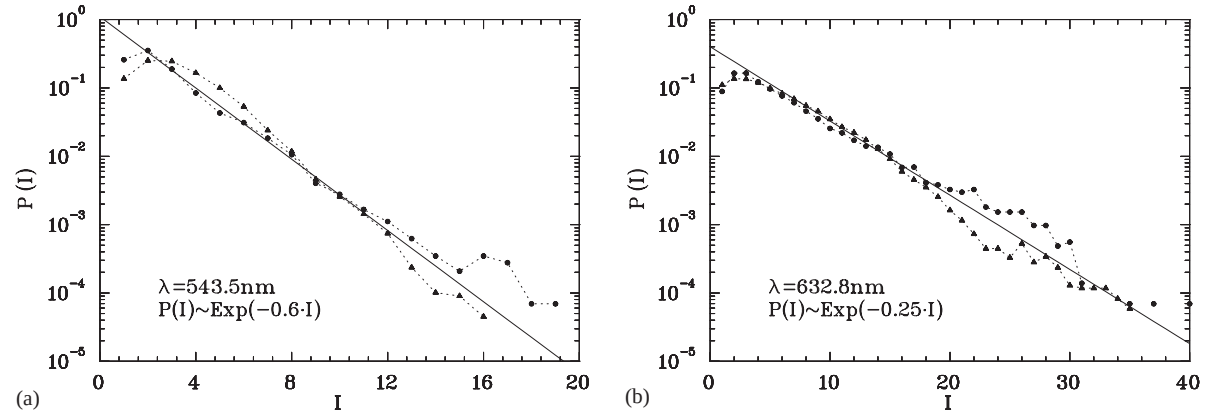

Fig. 2. The averaged local-field distributions $P(I)$ calculated for (a) $\lambda = 543$ nm; (b) $\lambda = 633$ nm. In both graphs the circles correspond to the theoretical PDF while the triangles are the corresponding experimental data. The solid line represents the exponential fit.

theory as well as a dramatic change in the PDF after averaging. This effect is due to the fact that in the averaging procedure we collect the field from a considerably large area ($120 \times 120\,nm^2$) in which the local field vector changes sign rapidly from point to point. As a result, we see a dramatic decrease of the local field enhancement I and a change in the shape of the distribution from lognormal to the exponential. Similar distribution functions were obtained in a previous work [13] but at that time the underlined physics was not clear. In connection to the scaling theory [2,3], it is important to note that the tail of the distribution for the red light in Fig. 2b shows the existence of local fields with an enhancement factor up to 40, which is two times larger compared to the green light (Fig. 2a). Such an increase of the average enhancement for the longer wavelength is a major prediction of the scaling theory [2,3] and is now confirmed through comparison between experimental measurements and exact numerical calculations.

In conclusion, by utilizing a new exact method we have confirmed the existence of strong enhancement of the local field in metal–dielectric films. The local field for $p = p_c$ is found to have a lognormal distribution. For lower (or higher) metal concentrations we obtain a single dipole field scaling region in the PDF. We also compare our theoretical finding with the experimental data extracted from NSOM images of metal–dielectric films. We found good agreement between the experimental and theoretical PDF.

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