Stimulated Emission of Surface Plasmon Polaritons

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We have observed laserlike emission of surface plasmon polaritons (SPPs) decoupled to the glass prism in an attenuated total reflection setup. SPPs were excited by optically pumped molecules in a polymeric film deposited on the top of a silver film. Stimulated emission was characterized by a distinct threshold in the input-output dependence and narrowing of the emission spectrum. The observed stimulated emission and corresponding compensation of the metallic absorption loss by gain enables many applications of metamaterials and nanoplasmonic devices.

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Photonic metamaterials, engineered composites with unique electromagnetic properties, have become in recent years a hot research topic because of their interesting physics and exciting potential applications, which include imaging with subdiffraction resolution [1–5], optical cloaking [6,7], and nanolasers [8–10]. Localized surface plasmons (SPs) and propagating surface plasmon polaritons (SPPs) play a key role in the design of the majority of metamaterials. Unfortunately, in contrast to mid- and far-IR structures [11,12], the performance of optical SP- and SPP-based systems is fundamentally limited by absorption loss in metal, which causes a reduction of the quality factor of SPs and shortening of the propagation length of SPPs. The solution to the loss problem, which has been proposed over the years in a number of publications [13–16], is to add an optical gain to a dielectric adjacent to the metal. A substantial enhancement by optical gain of localized SPs in aggregated silver nanoparticles, evidenced by a sixfold increase of the Rayleigh scattering, was demonstrated in [17,18]. A principal possibility to offset SPP loss by gain has been experimentally shown in Ref. [19], and the optical gain $\sim 420\ \mathrm{cm}^{-1}$ sufficient to compensate $\sim 30\%$ of the SPP internal loss in a silver film was achieved in Ref. [20]. Here we report the experimental observation of the stimulated emission of SPPs at optical frequency. Our work proves that the compensation of SPP loss by gain is indeed possible, opening the road for many practical applications of nanoplasmonics and metamaterials. Besides resolving one of the fundamental limitations of modern nanoplasmonics, the observed phenomenon adds a new emission source to the "toolbox" of active optical metamaterials. The obtained SPP stimulated emission is somewhat related to the theoretically proposed SPASER [21], the device analogous to laser designed to generate localized SPs. However, the existence of any feedback mechanism in our system remains questionable.

SPPs are electromagnetic waves coupled to oscillations of free-electron plasma, which propagate at the interface between metal (ε_1) and the adjacent to it dielectric (ε_2), Fig. 1(a). SPPs are confined to the proximity of metal-dielectric interface and decay exponentially in both media. The wave vector of the SPP propagating in the x direction is given by the expression $k_{\mathrm{SPP}} = \frac{\omega}{c}\sqrt{(\varepsilon_1 \cdot \varepsilon_2)/(\varepsilon_1 + \varepsilon_2)}$, where ω is the frequency and c is the speed of light [22]. SPPs can be excited, for example, by a p polarized light incident onto metallic film from the side of a glass prism at the critical angle θ_0, at which the projection of the wave vector of phonon to the x axis, $k_x^{\mathrm{phot}} = \frac{\omega}{c} n_0 \sin\theta_0$, is equal to k_{SPP}, Fig. 1(a). Once excited, SPPs propagate along the metallic surface, simultaneously decoupling to the prism at the same resonant angle θ_0.

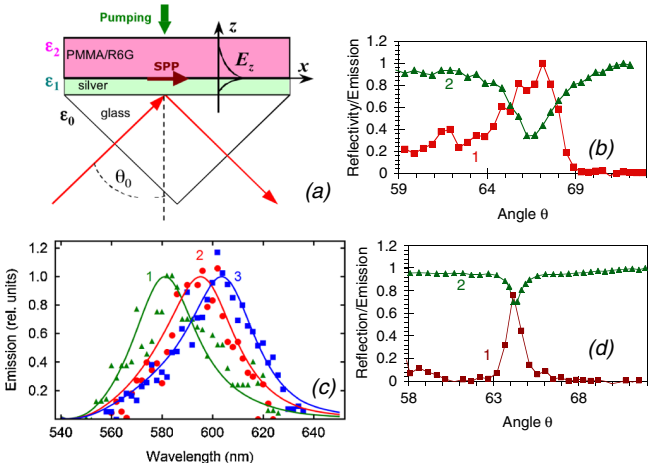

FIG. 1 (color online). (a) Experimental sample; excitation and decoupling of SPP. (b) Angular profile of emission of scattering-induced SPPs (trace 1) and the angular profile of reflectivity (trace 2); $\lambda = 575$ nm. (c) Spectra of SPP spontaneous emission decoupled at different angles θ; characters—experiment; solid lines—simulations; triangles and trace $1 - \theta = 67.17°$, circles and trace $2 - \theta = 66.14°$, squares and trace $3 - \theta = 65.62°$. The thickness of the silver film is 57 nm. (d) Angular profile of emission of scattering-induced SPPs (trace 1) and the angular profile of reflectivity (trace 2). $\lambda = 632.8$ nm.

In this work, 39–81 nm silver films were deposited on the glass prism with the index of refraction $n_0 = \sqrt{\varepsilon_0} = 1.7835$ and then coated with $1 - 3$ μm polymethyl methacrylate (PMMA) films doped with rhodamine 6G (R6G) dye in concentration 2.2×10^{-2} M, Fig. 1(a). The same dye-doped polymer was used as a gain medium of random laser in Ref. [23] and in our earlier study of the compensation of the SPP loss by gain [20]. The smaller thickness of the PMMA/R6G film used in this Letter in comparison to that in Ref. [20], allowed for a stronger pumping of dye molecules in the layer adjacent to the silver surface, as explained below.

Four different sets of experiments, numerated as (1)–(4) below, have been performed in the basic setup of Ref. [20] using the combination of the cw multiple-wavelengths He-Ne laser, Q switched second harmonic Nd:YAG laser, and tunable optical parametric oscillator (OPO, $t_{\text{pulse}} \approx 5$ ns).

(1) In the first set of measurements, used primarily for calibration purposes, we excited SPPs from the bottom of the prism and measured the reflectivity of the sample R as a function of the incidence angle θ [traces 2 in Figs. 1(b) and 1(d)]. This was done at a variety of wavelengths ranging from 532 to 632.8 nm at which decoupled SPPs were later studied in the experiments described below. At the resonance angle θ_0, the energy of incident light was transferred to SPPs, yielding a minimum in the reflectivity profile $R(\theta)$ [22]. This standard experiment accompanied by theoretical modeling [20,22] allowed us to determine the dielectric constants of the particular silver films studied. In the overall passive systems (well below the threshold), the width of the reflectivity profile $R(\theta)$ corresponds to the propagation length of SPP, $L = [2(\gamma_i + \gamma_r)]^{-1}$, with γ_i and γ_r being intrinsic losses due to material absorption and radiation losses due to SPP decoupling to the prism, respectively.

In the remaining experiments, the samples were excited from the PMMA side at nearly normal angle of incidence [see arrow in Fig. 1(a)], and the SPPs were excited either via scattering or via PMMA emission.

(2) Unintentional scatterers are always present in polymeric films and can even provide for feedback in polymer random lasers [24]. In our system scatterers enable excitation of surface plasmon polaritons via coupling of incident light into SPP modes. Experimentally, SPPs were excited via pumping the PMMA film (at $\lambda = 543.5$, 575.0, and 604.6 nm), and the intensity of light I decoupled to the prism was studied as a function of angle θ. The angular profile of the decoupled light intensity $I(\theta)$ had a maximum at almost the same resonance angle θ_0, for which $R(\theta)$ had its minimum, Fig. 1(b). This confirms that the detected light was, indeed, due to pumping-induced SPPs.

(3) In the third set of experiments, SPPs were excited via emission of R6G molecules in the PMMA film. The samples were pumped at relatively low fluence at the wavelength $\lambda = 532$ nm, corresponding to the absorption maximum of R6G. The laser light excited dye molecules in the PMMA/R6G volume, in particular, in the vicinity of the silver film where the pumping-induced SPPs are confined. Excited dye molecules, in turn, partly emitted to SPP modes at corresponding frequencies. The SPPs excited by optically pumped molecules (reported earlier in Refs. [25,26]) got decoupled to the prism at the angles corresponding to the SPPs' wave numbers. At low pumping intensity, the SPP spectra recorded at different angles θ qualitatively resembled the R6G spontaneous emission spectrum modulated by the SPP decoupling function, Fig. 1(c). Furthermore, the angular emission profiles $I(\theta)$ recorded at different wavelengths matched the reflectivity profiles $R(\theta)$, Fig. 1(d). This confirms that the observed emission was, in fact, due to decoupling of SPPs excited by pumped R6G molecules.

(4) In the fourth set of experiments, we increased the pumping intensity, and the character of the SPP emission excited via optically pumped dye molecules has changed dramatically.

(i) The emission spectra considerably narrowed in comparison to those at low pumping, Fig. 2(a).

(ii) The narrowed emission spectra peaking at ~602 nm became almost independent of the observation angle.

(iii) The dependence of the emission intensity (recorded in the maximum of the emission spectrum) on the pumping intensity was strongly nonlinear with the distinct threshold I_{th}, Fig. 2(b).

(iv) The value of the threshold I_{th} depended on the observation angle θ. The angular dependence $I_{\text{th}}(\theta)$ resembled the angular profile of the reflectivity $R(\theta)$, Fig. 2(c).

The experimental results above suggest the *stimulated* character of emission decoupled from SPP mode(s). To prove that the stimulated emission seen in our experiments comes from direct generation of SPPs rather than from lasing in purely photonic modes in the PMMA/R6G film (e.g., random lasing [24]) decoupled to prism via SPPs, we studied the emission collected from the back side of the prism as well as from glass slides with similar deposited films, close to the normal angle of incidence and at a grazing angle. At high pumping energy, the collected emission spectrally narrowed and demonstrated a threshold input-output behavior. However, the values of the thresholds for purely photonic modes (higher at nearly normal direction than at a grazing angle) were at least 4 times larger than the threshold in the case of SPPs decoupled to the prism, and the narrowed emission spectra had their maxima at wavelengths sometimes as short as ~584 nm. We thus conclude that the emission decoupled to the glass prism was generated by SPPs rather than originated in purely photonic modes within the PMMA/R6G layer above the silver film.

To further analyze the SPP emission observed in our experiments, we numerically solve Maxwell's equations with the transfer-matrix approach. In our simulations we first approximate the emitter by a point dipole and represent its field as a series of plane waves with well-defined

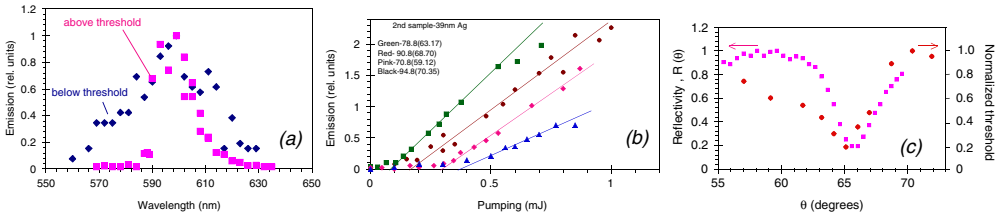

FIG. 2 (color online). (a) Spectra of the SPP emission recorded at $\theta = 68.7°$ at low pumping density 10.9 mJ/cm^2 (diamonds) and high pumping density 81.9 mJ/cm^2 (squares). (b) Input-output curves of SPP emission recorded at different angles θ. The thickness of the silver film is 39 nm. The diameter of the pumped spot is 2.16 mm, $\lambda = 602$ nm. Squares—$\theta = 63.17°$, circles—$\theta = 68.70°$, diamonds—$\theta = 59.12°$, triangles—$\theta = 70.35°$. Resonance angle—$\theta_0 = 65.56°$. (c). Dependence of the SPP stimulated emission threshold vs θ (circles) and the reflectivity profile (squares) measured at $\lambda \approx 604$ nm.

x components of the wave vectors through Fourier expansion. We then solve for propagation of individual components of this expansion using the transfer-matrix method (TMM) [27]. The resulting set of solutions represents the set of waveguide modes of open-waveguide structure formed by the finite-thickness metal film, the prism, and the gain material [28]. Correspondingly, the total emitted field coupled to the SPP is represented as a sum of these modes. This process allows us to directly calculate the field distribution in the system as well as to analyze angular and spectral distributions of the emitted signals below lasing threshold. The excellent agreement between experimental and theoretical SPP emission spectra at three different decoupling angles is shown in Fig. 1(c).

The TMM simulations, assuming linear behavior of the system in the frequency domain, are inapplicable near and above the lasing threshold. To qualitatively assess the onset of lasing oscillations, we use the following Fourier-transform-based approach. We first assume that SPP propagating in the x direction and decaying along its propagation is characterized by the complex wave vector $k_x = k_x' + ik_x''$, such that

$$E = E_0 e^{ik_x' x} e^{-k_x'' x} \tag{1}$$

where E is the SPP electric field and E_0 is its amplitude at $x = 0$. The spectrum of this SPP in a wave number domain is given by the Fourier transform

$$E(k) = \frac{1}{\pi} \int_0^{x'} E(x) e^{-ikx} dx = \frac{1}{\pi[-k_x'' + i(k_x' - k)]}, \tag{2}$$

where $x' = \infty$. Thus, similar to the case of TMM calculations described above, a single leaky SPP can be represented by a linear combination of open waveguide modes. Each of these modes is formed by the SPP coupled to two plane waves (incoming and outgoing) propagating at given angle θ in the prism [28]. The relative contribution of each mode to total absorption/emission of the system, given by Eq. (2), corresponds to Lorentzian distribution of decoupled light intensity about the resonant value of the wave vector and, in particular, determines the shape of the dip in the reflectivity profile $R(\theta)$, which is routinely recorded in SPP experiments in the attenuated total reflection geometry, Fig. 1(a).

When gain in the system overcomes loss, the negative sign in the second exponent of Eq. (1) changes to positive, which corresponds to exponential increase of the SPP intensity. In this case, if the upper limit of integration in Eq. (2) is set to be equal to infinity, the integral diverges, which physically corresponds to the fact that no steady-state gain can exist (or be physically supported by any source of pumping) in an infinitely large system. However, if the upper limit of integration is set at a finite value (the condition, which simulates a pumped spot of a finite size) then the integral can be readily solved analytically.

The Lorentzian-like spectrum of SPP emission $I_{\mathrm{SPP}}(k) \propto |E(k)|^2$, calculated for SPP propagation with amplification, has a maximum at the resonance wave number k_x', Fig. 3(a), in agreement with the experimentally observed reduction of the SPP lasing threshold at the resonant angle, Fig. 2(c). When emission intensities $I_{\mathrm{SPP}}(k)$ calculated at fixed wave vector k_x' and different values of gain k_x'' (pumping energies) are plotted against k_x'', the dependence, characterized by a distinct threshold, has a qualitative similarity with input-output curves measured experimentally, Figs. 2(b) and 3(b). Knowing the concentration of R6G molecules in the film (1.3×10^{19} cm^{-3}), absorption and emission cross sections of R6G ($\sigma_{abs}^{\lambda=532\ \mathrm{nm}} = 4.3 \times 10^{-16}$ cm^2, $\sigma_{em}^{\lambda=600\ \mathrm{nm}} = 1.9 \times 10^{-16}$ cm^2), and a lifetime of excited R6G molecules at given concentration of dye,

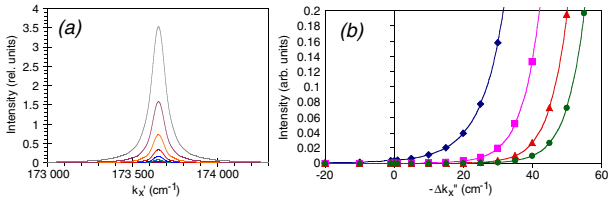

FIG. 3 (color online). (a) Calculated SPP spectra in the wave number domain. The values of gain in the SPP system (from high to low) correspond to $k_x'' = -50, -45, \ldots, -10, -5, -1, 0$ cm^{-1}. $\varepsilon_0 = n_0^2 = 3.18$, $\varepsilon_1 = -13.6 + i0.75$, $\varepsilon_2 = 2.25$; $\lambda = 594.1$ nm). The thickness of the silver film 39 nm. (b) Input-output curves of SPP emission calculated above the threshold at $k_x' = 173\,660$ cm^{-1} (close to the resonance)—diamonds, 173 740 cm^{-1}—squares, 173 860 cm^{-1}—triangles, and 174 000 cm^{-1}—circles.

$\tau = 1$ ns [29], we were able to evaluate (following Ref. [20]) the experimental threshold gains to be of the same order of magnitude as the theoretically predicted ones satisfying the condition $(\gamma_i + \gamma_r) = 0$. Thus, although nonlinear dependence of the SPP intensity on the pumping intensity and narrowing of the emission spectrum are expected even below the threshold, a good agreement between the theoretical and the experimental results serves as a strong indication that the observed emission is due to stimulated emission of SPPs in a regime when the total gain in the system exceeds the total loss.

To summarize, we have studied SPPs excited by emission of optically pumped R6G molecules and by direct scattering of pumping light in a polymeric film in the attenuated total reflection setup. We have observed laserlike emission of SPPs decoupled to the glass prism. The input-output dependence had a distinctive threshold and the emission spectrum narrowed considerably above the threshold. The threshold and the overall emission intensity strongly depended on the SPP decoupling angle. Thus, the threshold was minimal and the emission intensity was maximal at the resonance condition, at which the wave vector of the SPP k_{SPP} was equal to the projection of the photon wave vector to the metal-dielectric interface k_x^{phot}. This behavior is in good agreement with the model considering SPP propagation with amplification, when the total gain in the system exceeds the total loss. That is why we ruled it out as a possible source of the laserlike SPP behavior. The experimental thresholds of SPP stimulated emission had the same order of magnitude as the theoretically predicted ones. The observed phenomenon may be relevant to the SPASER proposed in Ref. [21]. However, the existence of the stimulated emission feedback, which is a key element of the SPASER, was not confirmed in our system. Moreover, in contrast to the SPASER that generates localized SPs, our system generates propagating SPP waves.

Note that unintentional scatterers, which are common to polymeric films, provide for stimulated emission feedback in many polymer random lasers [23,24]. The same scattering centers plus scatterers associated with the metallic film can potentially provide for feedback of the SPP stimulated emission. Although this feedback is possible and even likely, we do not have experimental evidence of its existence. The results of this ongoing study will be published elsewhere.

The demonstrated phenomenon adds a new stimulated emission source to the toolbox of nanophotonic materials and devices and proves that total compensation by metamaterials' loss by gain is, indeed, possible. By replacing dye molecules with quantum dots, one can reduce the photobleaching and make the system even more practical.

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