Modified light emission from emitters coupled to long-range guided modes in strongly absorbing layers

Christophe Arnold,[1*] **Yichen Zhang,**[1] **and Jaime Gómez Rivas,**[1,2]

[1] *Center for Nanophotonics, FOM Institute AMOLF, c/o Philips Research Laboratories, High Tech Campus 4, 5656 AE Eindhoven, The Netherlands*

[2] *COBRA Research Institute, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

** christophe.arnold@lpn.cnrs.fr*

Abstract: We demonstrate the near-field coupling and energy transfer between photoexcited dye molecules and guided modes in layers of strongly absorbing dielectrics. The dye molecules decay by exciting long-range guided modes (LRGMs) in a thin layer of chalcogenide glass. These modes can exist in spite of the very large absorption of the material forming the layer. The LRGMs are detected by coupling then out to free space radiation through a prism in the Krestschmann configuration. By calculating the dissipated power of a dipole, representing a dye molecule, in the vicinity of the absorbing thin film, we show that there is a large probability of decay exciting LRGMs. This probability can reach 35% for perpendicularly oriented dipoles. The demonstration of the excitation of LRGMs in thin films of absorbing dielectrics by near-field coupling of excited molecules opens the possibility to compensate for the losses in the propagation of these modes.

OCIS codes: (130.2790) Guided waves; (240.6690) Surface waves; (230.7370) Waveguides; (260.3800) Luminescence

References and links

1. P. Berini, "Long-range surface plasmon polaritons," Adv. Opt. Photon. **1**, 484–588 (2009).
2. R. Haïdar, G. Vincent, S. Collin, N. Bardou, N. Guérineau, J. Deschamps, and J.-L. Pelouard, "Free-standing subwavelength metallic gratings for snapshot multispectral imaging," Appl. Phys. Lett. **96**, 221104 (2010).
3. S. Kawata, Y. Inouye, and P. Verma, "Plasmonics for near-field nano-imaging and superlensing," Nat. Photon. **3**, 388–394 (2009).
4. G. Nenninger, P. Tobika, J. Homola, and S. Yee, "Long-range surface plasmons for high-resolution surface plasmon resonance sensors," Sens. Actuator B-Chem. **74**, 145–151 (2001).
5. G. J. Kovacs, "Surface polariton in the atr angular spectra of a thin iron film bounded by dielectric layers," J. Opt. Soc. Am. **68**, 1325–1332 (1978).
6. F. Yang, J. R. Sambles, and G. W. Bradberry, "Long-range coupled surface exciton polaritons," Phys. Rev. Lett. **64**, 559–562 (1990).
7. F. Yang, J. R. Sambles, and G. W. Bradberry, "Long-range surface modes supported by thin films," Phys. Rev. B **44**, 5855–5872 (1991).
8. C. Arnold, Y. Zhang, and J. Rivas, "Long range surface polaritons supported by lossy thin films," Appl. Phys. Lett. **96**, 113108 (2010).
9. Y. Zhang, C. Arnold, P. Offermans, and J. G. Rivas, "Surface wave sensors based on nanometric layers of strongly absorbing materials," Opt. Express **20**, 9431–9441 (2012).
10. V. Giannini, Y. Zhang, M. Forcales, and J. G. Rivas, "Long-range surface polaritons in ultra-thin films of silicon," Opt. Express **16**, 19674–19685 (2008).

#174891 - $15.00 USD Received 24 Aug 2012; revised 19 Nov 2012; accepted 19 Nov 2012; published 28 Nov 2012

11. D. Koller, A. Hohenau, H. Ditlbacher, N. Galler, F. Reil, F. Aussenegg, A. Leitner, E. List, and J. Krenn, "Organic plasmon-emitting diode," Nat. Photon. **2**, 684–687 (2008).
12. R. J. Walters, R. V. A. van Loon, I. Brunets, J. Schmitz, and A. Polman, "A silicon-based electrical source of surface plasmon polaritons," Nat. Mater. **9**, 21–25 (2010).
13. J. Seidel, S. Grafstrom, and L. Eng, "Stimulated emission of surface plasmons at the interface between a silver film and an optically pumped dye solution," Phys. Rev. Lett. **94**, 177401 (2005).
14. M. Ambati, S. H. Nam, E. Ulin-Avila, D. A. Genov, G. Bartal, and X. Zhang, "Observation of stimulated emission of surface plasmon polaritons," Nano Lett. **8**, 3998–4001 (2008).
15. M. A. Noginov, G. Zhu, M. Mayy, B. A. Ritzo, N. Noginova, and V. A. Podolskiy, "Stimulated emission of surface plasmon polaritons," Phys. Rev. Lett. **101**, 226806 (2008).
16. I. De Leon and P. Berini, "Amplification of long-range surface plasmons by a dipolar gain medium," Nat. Photon. **4**, 382–387 (2010).
17. M. C. Gather, K. Meerholz, N. Danz, and K. Leosson, "Net optical gain in a plasmonic waveguide embedded in a fluorescent polymer," Nat. Photon. **4**, 457–461 (2010).
18. P. Berini and I. De Leon, "Surface plasmon-polariton amplifiers and lasers," Nat. Photon. **6**, 16–24 (2012).
19. R. R. Chance, A. Prock, and R. Silbey, "Lifetime of an excited molecule near a metal mirror: Energy transfer in the eu[sup 3 +]/silver system," J. Chem. Phys. **60**, 2184–2185 (1974).
20. G. W. Ford and W. H. Weber, "Electromagnetic interactions of molecules with metal surfaces," Phys. Rep. **113**, 195–287 (1984).
21. A. Archambault, F. Marquier, J.-J. Greffet, and C. Arnold, "Quantum theory of spontaneous and stimulated emission of surface plasmons," Phys. Rev. B **82**, 035411 (2010).
22. L. Novotny, "Allowed and forbidden light in near-field optics. i. a single dipolar light source," J. Opt. Soc. Am. A **14**, 91–104 (1997).
23. A. Sommerfeld, "Uber die ausbreitung der wellen in der drahtlosen telegraphie," Ann. Phys. **28**, 665-736 (1909).
24. J. Kalkman, H. Gersen, L. Kuipers, and A. Polman, "Excitation of surface plasmons at a SiO_2/Ag interface by silicon quantum dots: Experiment and theory," Phys. Rev. B **73**, 075317 (2006).

1. Introduction

Long-range guided modes (LRGMs) are surface modes guided along thin layers embedded in dielectrics. A thoroughly studied type of LRGMs are long-range surface plasmon polaritons (LRSPPs) supported by metallic layers. On a metallic thin film, the surface plasmon polaritons supported by the two interfaces can couple, giving rise to coupled polaritons with a symmetric and antisymmetric field distribution with respect to the middle plane of the layer. These polaritons are known as short-range and long-range surface plasmon polaritons, respectively. The reduction of the energy density inside the absorbing layer for the LRSPPs, gives rise to a decrease in the optical loss and a long propagation length [1]. The confinement of the electromagnetic field of LRSPPs close to the surface of the layer and their long propagation length explain the large number of applications which have been proposed for these modes [1]: We can cite the guiding of light in integrated optical circuits [1], colour filters [2], imaging systems [3] or optical sensors [4].

In 1978, Kovacs showed that LRGMs can be also supported by thin films of highly absorbing metals [5]. Yang *et al.* generalized the concept of LRGMs to strongly absorbing dielectrics [6], i.e., dielectrics with an imaginary component of the permittivity much larger than their real component. A general classification of LRGMs in thin layers with different values of the permittivity was presented in Ref. [7] . Similarly to LRSPPs, LRGMs originates from the coupling of surfaces waves supported on each interface of a thin film. This coupling reduces the energy density inside the thin film and provides the long-range propagation characteristics of these modes [7–9]. Even though the characteristics of LRGMs in terms of confinement and propagation are not as good as those of LRSPPs, LRGMs in strongly absorbing thin layers can propagate 10's to 100's of vacuum wavelengths along the layer, while still being confined within a wavelength to the surface [10].

For the development of applications, sources of surface modes and LRSPPs are required. First demonstrations of electrical sources of plasmonic waves have been shown recently [11, 12]. Also, the compensation of the optical loss of these modes during their propagation

#174891 - $15.00 USD Received 24 Aug 2012; revised 19 Nov 2012; accepted 19 Nov 2012; published 28 Nov 2012

by stimulated emission would lift the major limitation that hampers their applicability. This explains the growing interest on this topic [13–18]. For these reasons, the interaction between plasmonic surface waves and emitters is an important field of research, which has been studied both from the classical [19, 20] and quantum point of views [21]. This research started with the investigation of the acceleration of emission of emitters close to metallic mirrors by excitation of surface plasmon polaritons [19, 20]. The interaction between LRGMs supported by very lossy thin films with emitters still needs to be explored.

In this article, we demonstrate the excitation of LRGMs in a layer of chalcogenide glass by near field coupling of photoexcited dye molecules. The chalcogenide glass is a strongly absorbing dielectric, with an imaginary component of the permittivity larger than its real component over the whole visible spectrum. Electrodynamic calculations of the dissipated power by classical dipoles placed at a certain distance to the layer reproduce the measurements. We find that a significant fraction of the power goes on the excitation of LRGMs. Our measurements represent the first step towards loss compensation on the propagation of long-range modes in lossy dielectrics.

2. Experimental demonstration of LRGMs emission

The thin film supporting LRGMs was prepared as follows: The substrate of the sample is a SCHOTT F2 glass plate. We sputtered a layer of nitrided silicon oxyde (SiON) on this substrate with a thickness of 300 nm. The refractive index of this material is close to the refractive index of poly(methyl methacrylate) (PMMA) (n$\sim$1.48), used as matrix for the dye. A layer of chalcogenide glass $Ge_{17}Sb_{76}Te_7$ (GST) with a thickness of 25 nm was sputtered in its amorphous phase on top of the SiON. This layer is the lossy thin film that supports the guided mode. The complex permittivity of GST was obtained from ellipsometry measurements and it is displayed in Fig 1(a). We sputtered a 100 nm thick layer of SiON on top of the GST layer. The role of this layer is to prevent the quenching of the dye emission due to the vicinity of the lossy thin film. On top of the SiON layer, we deposited by spin-coating a layer of PMMA with a thickness of 90 nm, doped with dye molecules (Lumogen F Red 305, BASF). The concentration of the dye molecules in the PMMA layer is 2.5×10^{-2}M. These dye molecules have a broad absorption band ($500 - 600$ nm) and their emission spectrum extend from 580 to 750 nm, with a maximum at 613 nm. We spin-coated a second layer of PMMA with a thickness of 500 nm, but without dye molecules. This layer reduces the disturbance of the air/PMMA interface on the excitation and propagation of the LRGM.

A SCHOTT-F2 glass prism was used to couple out the LRGMs to free space radiation that could be detected. The prism was brought into optical contact with the substrate of the sample with a refractive index matching liquid (Cargille, n=1.62). The LRGMs excited by the dye molecules propagate along the GST film, decaying evanescently into the SiON and PMMA layers. Due to the higher index of refraction of F2 glass, the evanescent field couples to free space radiation through the prism (Kretschmann configuration). The setup used for the experiments is depicted in Fig 1(b). We pumped the dye by illuminating the sample from the PMMA side with the beam of a supercontinuum light source, using a band-pass filter (530 ± 5 nm) to narrow the pump spectrum. The fluorescence was measured with a fiber coupled spectrometer that could be automatically rotated around the sample in the side of the prism. A polarizer placed between the prism and the spectrometer was used to select the polarization before detection. We normalized the measurements by dividing the fluorescence by a reference obtained at the same angle and wavelength and in the same Kretschmann configuration. The reference sample consists of a F2 substrate with the same layered structure as in the sample, except for the absence of the GST layer.

To control the quality of the sample, as well as the existence of LRGMs supported by the

#174891 - $15.00 USD Received 24 Aug 2012; revised 19 Nov 2012; accepted 19 Nov 2012; published 28 Nov 2012

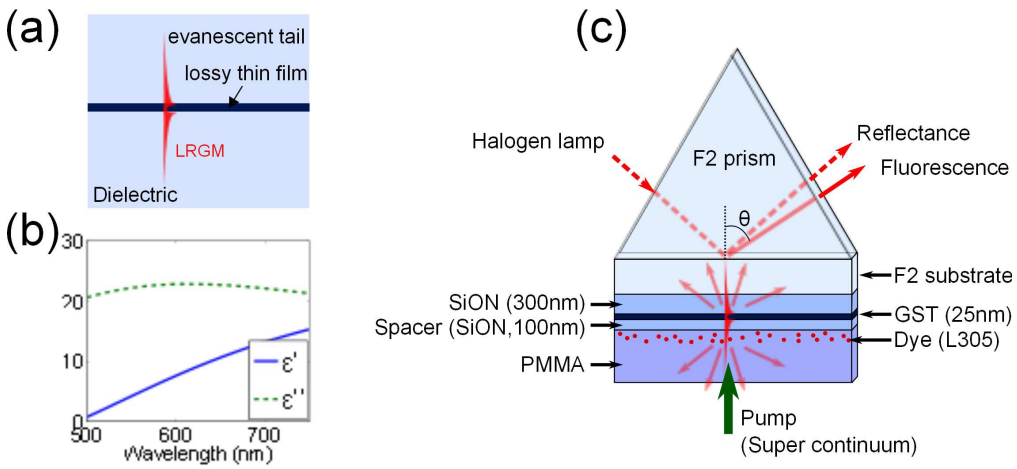

Fig. 1. (a) Schematic representation of the field intensity distribution of a LRGM around a thin layer of a strongly absorbing material. (b) Real (solid line) and imaginary components(dash line) of the permitttivity of $Ge_{17}Sb_{76}Te_7$. (c) Schematic representation of the setup. From the top to the bottom of the structure: F2 prism, F2 substrate optically matched to the prism through refractive index matching liquid (not shown), dielectric layer of SiON (300 nm), $Ge_{17}Sb_{76}Te_7$ thin film (25 nm), SiON (100 nm), PMMA layer with dye (90 nm) and PMMA layer (500 nm). For the fluorescence measurements, the dye molecules are pumped from the bottom with a supercontinuum light source and the emission is collected from the side of the prism. For the specular reflectance measurements, the beam from a halogen lamp is incident onto the sample through the prism.

GST film, we have performed attenuated total internal reflection measurements. A collimated beam from a halogen lamp was used to illuminate the sample from the prism and the specular reflection was detected (see Fig. 1(b)). The sample and detector (fiber-coupled spectrometer) were rotated with computer controlled $\theta - 2\theta$ rotation stages. Figure 2(a) shows the specular reflectance measured for a *p*- polarized incident beam. The critical angle for total internal reflection at the F2-SiON interface is 66°. The evanescently transmitted amplitude at angles larger than the critical angle can resonantly couple to LRGMs in the GST film. This coupling leads to a reduction of the total internal reflection that can be observed around 68° in Fig. 2(a). We also see a dip in the reflectance around 62°, which comes from a Fabry-Pérot resonance into the PMMA layer. Figure 2(b) displays the reflectance measured for s- polarized incident light. The LRGM resonance is not present for this polarization, given that this mode is only supported for *p*- polarization [6, 7, 10]. The resonance at angles lower than 65° is due to a Fabry-Pérot resonance into the PMMA layer. Figures 2(c) and (d) display the specular reflectance calculated with the transfer matrix method for *p*- and *s*- polarization, respectively. For these calculations we have used the values of the refractive indices of the layers determined separately with ellipsometry measurements (not shown here). The thicknesses of the different layers have been used as fitting parameters to obtain a good agreement between the calculation and the measurements. The values of the thicknesses obtained from the fits are 300 ± 30 nm, 24 ± 2 nm, and 690 ± 50 nm for the SiON, GST and SiON plus PMMA layers, respectively. These values agree with the nominal thicknesses used for the sample fabrication.

#174891 - $15.00 USD Received 24 Aug 2012; revised 19 Nov 2012; accepted 19 Nov 2012; published 28 Nov 2012

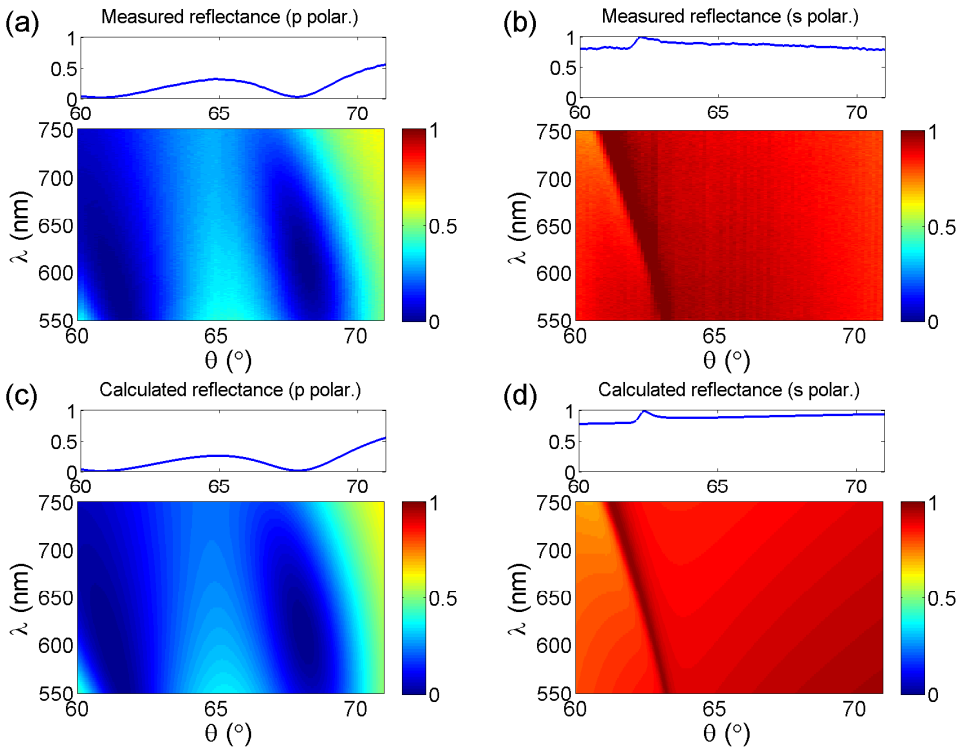

Fig. 2. (a) and (b) are the measured specular reflectance spectra, normalized to the reference, as a function of the angle on incidence of the multilayered structure for *p*- and *s*- polarizations, respectively. (c) and (d) are the calculated reflectance for *p*- (c) and *s*- (d) polarizations. The upper insets are the specular reflectance measurements at $\lambda = 650$ nm. Permittivity of each layer at 650 nm: $\varepsilon_{GST} = 8.2322 + 20.528i$, $\varepsilon_{PMMA} = 2.2103$, $\varepsilon_{SiO_2} = 2.1947$ and $\varepsilon_{F2} = 2.6055$.

The fluorescence normalized to the reference are depicted in Figs. 3 for *p*- (a) and *s*- (b) polarizations. For *p*- polarization, we obtain a band of enhanced fluorescence at the same angle of emission at which the minimum of specular reflectance, corresponding to the excitation of LRGM, is measured. The enhancement of the fluorescence is the result of the energy transfer of the photoexcited dye molecules to the guided modes and the subsequent outcoupling of these modes into radiation by the the prism. It is interesting to note that there is no enhancement of fluorescence through the Fabry-Pérot resonance. It is thus more probable for the dye to decay into LRGM. As expected, the band of enhanced emission associated to LRGM is not present in the fluorescence measurements of *s*-polarized light (Fig. 3(b)). For this polarization, the guided mode in the PMMA layer leads to a small enhancement of fluorescence for angles lower than 63°. The weak band of enhanced fluorescence at angles larger than 67° is attributed to a parasite reflection in the setup.

#174891 - $15.00 USD Received 24 Aug 2012; revised 19 Nov 2012; accepted 19 Nov 2012; published 28 Nov 2012

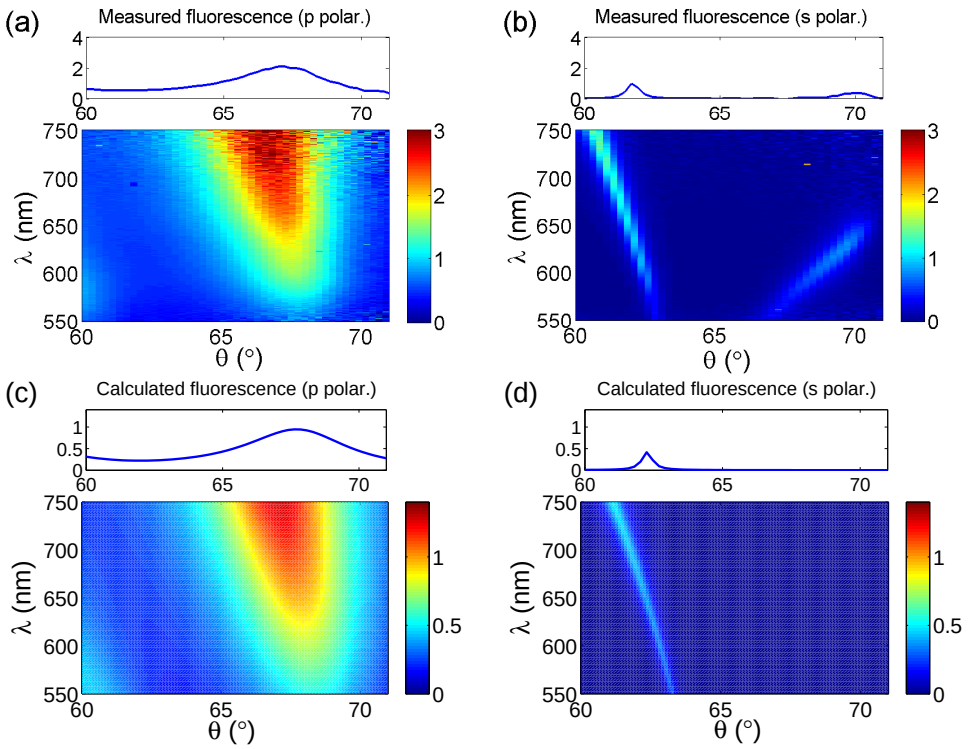

Fig. 3. (a) and (b) are the measured fluorescence spectra of the dye molecules of the multilayered structure as a function of the angle of emission for *p*- and *s*- polarizations respectively. (c) and (d) are the calculated fluorescence spectra for *p*- and *s*- polarizations. The upper insets correspond to the fluorescence emission at $\lambda = 650$ nm.

Although spontaneous emission is a quantum mechanical phenomenon, it is possible to accurately calculate the fluorescence of emitters by using classical electrodynamic theory. In particular, fluorescence calculations of emitters close to or inside planar multilayer structures have been studied thoroughly [20,22], beginning with Sommerfeld's pioneer works [23]. These calculations consist in expanding the field emitted by an harmonic oscillating dipole in cylindrical coordinates (Sommerfeld expansion) and to calculate the field in the whole system by means of the Fresnel reflection and transmission coefficients. Knowing the field at the dipole position, it is then possible to deduce its dissipated power, as well as fluorescence radiation pattern [22].

Figures 3(c) and (d) display the calculation of the normalized emission pattern corresponding to our experiment for *p*- and *s*- polarizations, respectively. The emission is calculated for an emitter randomly oriented in the PMMA layer. The fluorescence is normalized in the same way as the measurements of Figs. 3(a) and (b), i.e., by dividing the emission pattern to a reference without the GST film. The thicknesses and refractive indices of the different layers are the same as the values used for the calculation of the reflectance. In the experiment, the dye molecules are spread in a layer of 90 nm of PMMA, while in the calculations we only consider the radiated power of dipoles placed in the middle of the layer containing the dye. We get an excellent qualitative agreement between measurements and calculations. The calculation for *p*-polarization shows the presence of the band of enhanced emission corresponding to the excitation and outcoupling of LRGMs. This band is absent in the calculation of the emission for s-polarized light. The difference between experiments and calculations on the absolute value of the normalized emission can be attributed to the different intensity in the experiments of the

#174891 - $15.00 USD Received 24 Aug 2012; revised 19 Nov 2012; accepted 19 Nov 2012; published 28 Nov 2012

pump beam in the PMMA layer between the sample with the GST thin film and the reference sample. It is worth noting that the ratio between the maxima of *p*- and *s*- polarizations agrees remarkably well between measurements and calculations.

3. Decay probability calculations of emitters in the vicinity of absorbing thin films

We have also calculated the dissipated power or the decay probability of an emitter close to the GST thin film surrounded by PMMA (without prism). The dipole have several channels into which it can dissipate its energy: By emitting into free space radiation, by coupling to LRGMs or by absorption through lossy surface waves in the GST layer [24]. To determine the decay probability in each of these channels, we integrate the field components at the emitter's position over the out-of-plane wave vector. In this way, we obtain the field as a function of the in-plane wave number $k_{\|} = \frac{2\pi}{\lambda}\sin\theta$, where θ is the angle defined with respect to the sample normal. Integration of the total decay probability in different ranges of $k_{\|}$ allows to determine the probability of decay into the different channels. For $k_{\|} < k_0 n$ (where k_0 is the vacuum wave number and n the refractive index of the dielectric surrounding the GST layer), the dissipated power goes into radiation. Larger values of $k_{\|}$ correspond to evanescent field components. LRGMs have values of $k_{\|}$ close to $k_0 n$. For larger values of $k_{\|}$, the dissipated power goes into lossy surface waves. Figure 4(a) shows the decay probabilities to the different decay channels as a function of the distance between the dipole and the GST thin film. For this calculation, we consider an isotropically oriented emitter with a quantum efficiency of unity. The wavelength of the calculation is 600 nm. When the dipole is far from the GST layer, the dye has a probability of 100% to decay by emitting radiation. The decay probability into LRGMs and lossy surface waves increases as the distance to the layer is reduced. For a distance smaller than 80 nm, the absorption associated to lossy surface waves is the dominant decay channel. This dominant decay into lossy surface waves at small distances gives rise to a maximum decay probability into LRGMs of 12% at a distance of 120 nm to the layer. For dipoles oriented perpendicularly to the interfaces, this probability is larger, reaching 35% for the same distance (see Fig. 4(b)). This larger probability is due to the fact that for the perpendicular orientation, the dipole emits preferentially *p*-polarized light, whereas for isotropically or parallel orientation, a fraction of the radiated power goes into *s*- polarization, which can not participate in the excitation of LRGMs. We point out that this calculation has been obtained for a GST thin film of 25nm. A different thickness would change the confinement of the mode and so its coupling with the dipole, which would lead to a change of the decay probability. This change would also affect the other decay channels."

#174891 - $15.00 USD Received 24 Aug 2012; revised 19 Nov 2012; accepted 19 Nov 2012; published 28 Nov 2012

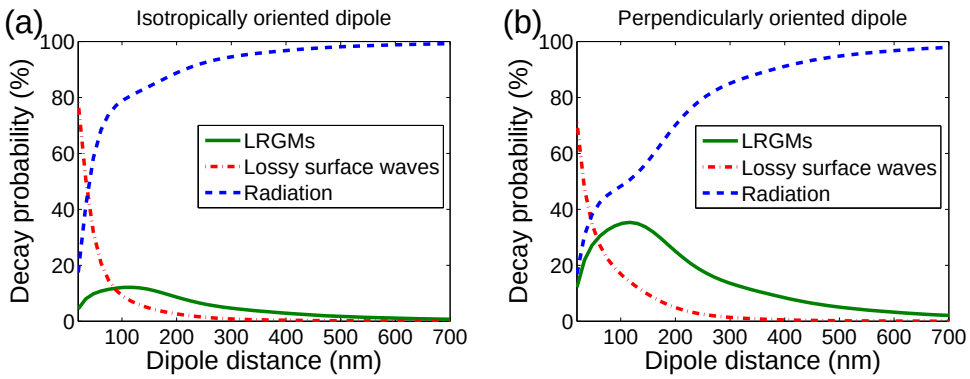

Fig. 4. Decay probability for an isotropically (a) and perpendicularly (b) oriented dipole as a function of the distance of the dipole to the GST thin film. The wavelength is 600 nm and the thickness of the layer is 25 nm. The curves represent the three different decay channels.

4. Conclusion

In conclusion, we have investigated the emission of photoexcited dye molecules in the vicinity of strongly absorbing thin films of chalcogenide (GST) glass. The excited molecules have a large probability (a maximum of 12% and 35% for randomly and perpendicularly oriented dipoles, respectively) of decaying transferring its energy to long-range guided modes (LRGMs). These modes are supported by the thin layer, in spite of the very large absorption of GST. Our demonstration of near-field coupling and energy transfer from dye molecules to guided modes in layers of strongly absorbing dielectrics constitutes the first step towards the compensation of losses in these modes.

Acknowledgments

This work was supported by the Netherlands Foundation Fundamenteel Onderzoek der Materie (FOM) and the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO), and is part of an industrial partnership program between Philips and FOM.

#174891 - $15.00 USD Received 24 Aug 2012; revised 19 Nov 2012; accepted 19 Nov 2012; published 28 Nov 2012