AIP | Applied Physics Letters

Gain assisted nanocomposite multilayers with near zero permittivity modulus at visible frequencies

Carlo Rizza, Andrea Di Falco, and Alessandro Ciattoni

Citation: Applied Physics Letters **99**, 221107 (2011); doi: 10.1063/1.3665414
View online: http://dx.doi.org/10.1063/1.3665414
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/99/22?ver=pdfcov
Published by the AIP Publishing

Gain assisted nanocomposite multilayers with near zero permittivity modulus at visible frequencies

Carlo Rizza,[1,2] Andrea Di Falco,[3] and Alessandro Ciattoni[2,a)]
[1]*Dipartimento di Fisica e Matematica, Universitá dell'Insubria, Via Valleggio 11, 22100 Como, Italy*
[2]*Consiglio Nazionale delle Ricerche, CNR-SPIN, 67100 Coppito L'Aquila, Italy*
[3]*School of Physics and Astronomy, University of St. Andrews, North Haugh, St. Andrews KY16 9SS, United Kingdom*

(Received 31 May 2011; accepted 6 November 2011; published online 30 November 2011)

We have fabricated a nano-laminate by alternating metal and gain medium layers, the gain dielectric consisting of a polymer incorporating optically pumped dye molecules. From standard reflection-transmission experiments, we show that, at a visible wavelength, both the real and the imaginary parts of the permittivity $\epsilon_\parallel$ attain very small values and we measure, at $\lambda = 604$ nm, $|\epsilon_\parallel| = 0.04$ which is 21.5% smaller than its value in the absence of optical pumping. Our investigation thus proves that a medium with a permittivity with very small modulus, a key condition promising efficient subwavelength optical steering, can be actually synthesized. © *2011 American Institute of Physics*. [doi:10.1063/1.3665414]

Epsilon-near-zero (ENZ) metamaterials are engineered materials with a very small real part of the dielectric permittivity. Their unique properties, enabling exotic light behavior, have recently been addressed both in the linear[1–3] and in the nonlinear regimes.[4–7] The ENZ condition can be easily achieved by alternating materials with negative (metals) and positive (dielectric) values of the real permittivity, to obtain an average value close to zero, for a given wavelength and polarization.[8,9] This effective medium approximation is only valid if the individual layers are much smaller than the wavelength, i.e., down to few nanometers in the optical range. However, few nanometers thin metal layers are generally accompanied by unwanted effects responsible for substantial material absorption as, for example, dislocation and island formation[10] and size-effects. As a result, it is necessary to use thicker layers and, consequently, adopt a more refined theoretical approach, accounting for spatial nonlocal corrections.[11,12]

On the other hand, while most of the research effort on ENZ metamaterials is focused on achieving a very small real part of the permittivity, we point out that its imaginary part plays a crucial role as well. Hence, the quantity to be minimised is $|\epsilon|$. In such generalized ENZ metamaterials, small permittivity changes would no longer be playing the role of a mere perturbation and can have a dramatic impact on optical propagation.[5] This condition would allow an extremely efficient external control (e.g., via optical nonlinearity, electro-optic effect, and acousto-optic effect), for example, to obtain very effective (low power) optical steering and light manipulation.[13] It is then clear that to exploit the full potential of generalized ENZ metamaterials, managing the imaginary part of the permittivity, i.e., adopting schemes for loss compensation is of pivotal importance. Various techniques and gain mechanisms have been proposed so far to achieve this goal. Examples are negative index materials with gain nanoconstituents,[14–16] negative dielectrics hosting quantum dots,[17–21] and surface plasmon polaritons excitation in the presence of optically pumped dye molecules.[22–25]

In this letter, we demonstrate experimentally that a metallo-dielectric nano-laminate can be designed to fulfill the generalized ENZ condition, for the polarization parallel to the layers' plane ($|\epsilon_\parallel| \ll 1$), at visible frequencies. We achieve control over $|\mathrm{Re}(\epsilon_\parallel)|$ by carefully choosing the layers' thickness, whereas we reduce $|\mathrm{Im}(\epsilon_\parallel)|$ by using an optically pumped organic dye. Even though nanometric, the layers' thicknesses are not very much smaller than the considered radiation wavelengths so that effective medium theory fails to provide an accurate description of the manufactured nano-laminate. On the other hand, our experimental findings are perfectly predicted by the approach of Elser *et al.*[11] which, based on a photonic crystal analysis, goes beyond the standard effective medium theory since it provides a description of the laminate valid for higher orders of layers' period to wavelength ratio. The multilayer stacks were fabricated by alternating layers of e-beam evaporated silver (20 nm) and spun polymethilmethacrylate (PMMA 495, from Microchem) (120 nm), on glass. The layers' thickness was measured with a Dektak stylus profiler, with accuracy better than 1 nm. The polymer included an optimized concentration of 1.5 mg/ml of Lumogen Red dye, with absorption peak at 565 nm and emission peak at ∼610 nm. The optimization was performed with independent experiments by measuring with an integrating sphere the emission efficiency of samples with a 100 nm thick film, with different concentrations, from 1 mg/ml to 6 mg/ml. We fabricated several samples with varying number of metal/polymer bilayers from 3 to 5. The transmission (T) and reflection (R) measurements (pertaining to the overall samples, i.e., laminate and glass substrate) were performed with polarized broadband light emitted by a tungsten lamp, all with normal incidence to the samples. T and R were collected with two independent silicon-based optical spectrometers, limiting the observed wavelength range to 500–1100 nm. The dye was then excited with a doubled Nd:Yag emitting cw light at 532 nm, with an average power of 200 mW. The samples were pumped at an angle (∼40° with respect to the normal) to avoid direct pump light reaching either of the spectrometers. To prevent the

a)Electronic mail: alessandro.ciattoni@aquila.infn.it.

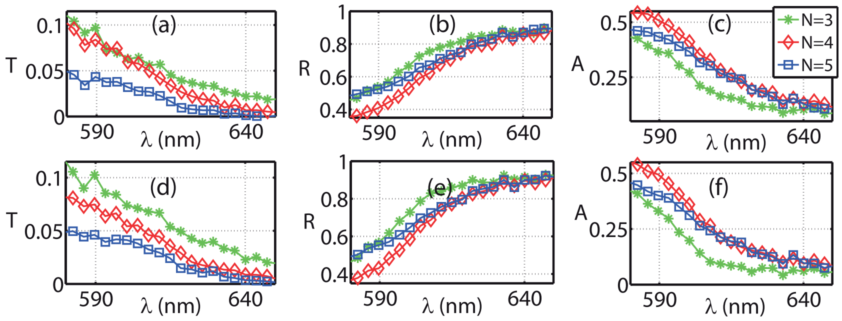

FIG. 1. (Color online) Measured transmittances (T), reflectances (R), and absorbances (A) of the samples made up of $N=3$, 4, 5 metallo-dielectric bilayers, without optical pumping (panels (a), (b), and (c)) and with optical pumping (panels (d), (e), and (f)).

tungsten lamp from exciting the dye, we filtered the incoming probe signal with a long pass filter with cutoff wavelength at 570 nm. To design our samples, we theoretically modelled the medium dielectric tensor $\epsilon = \mathrm{diag}(\epsilon_\parallel, \epsilon_\parallel, \epsilon_\perp)$, where according to Ref. 11,

$$\epsilon_\parallel = \frac{\epsilon_\parallel^{(0)}}{1-\Delta}. \tag{1}$$

Here, $\epsilon_\parallel^{(0)} = \frac{t_{Ag}\epsilon_{Ag}+t_{PMMA}\epsilon_{PMMA}}{t_{Ag}+t_{PMMA}}$ is the average of the metal and dielectric permittivities ϵ_{Ag} and ϵ_{PMMA}, respectively, $\Delta = \frac{(\epsilon_{Ag}-\epsilon_{PMMA})^2}{12\epsilon_\parallel^{(0)}}\left(\frac{t_{Ag}t_{PMMA}}{t_{Ag}+t_{PMMA}}\frac{2\pi}{\lambda}\right)^2$ and $\lambda = \frac{2\pi c}{\omega}$ is the vacuum wavelength. Note that $\epsilon_\parallel^{(0)}$ is the permittivity predicted by the standard effective medium theory and that Eq. (1) reduces to $\epsilon_\parallel = \epsilon_\parallel^{(0)}$ in the limit of very small layers' thicknesses t_{Ag} and t_{PMMA}. From the denominator of Eq. (1), it can be noted that the real and imaginary parts of the metal and the polymer are correlated. This effect is only predicted by this improved description of the effective medium and is confirmed below by the experimental evidence. Using the Lorentz-Drude model for the silver permittivity ϵ_{Ag} reported in Ref. 26 and setting $\epsilon_{PMMA} = 1.95$,[27] from Eq. (1), we obtain $\mathrm{Re}(\epsilon_\parallel) = 0.0002$ at $\lambda = 595.4$ nm, for the chosen t_{PMMA} and t_{Ag}.

The measured T and R of various samples with $N=3$, 4, 5 bilayers (both without and with optical pumping) are reported in Fig. 1 and such data have been used to retrieve the complex dielectric permittivity of the laminate. Specifically the retrieval procedure has been based on the relations $T = T_l T_{sub}(1+R_l R_{sub})$ and $R = R_l + T_l^2 R_{sub}$, where subscripts l and sub label the laminate (considered as a homogeneous medium) and the glass substrate, respectively. These relations have been derived by using the multiple scattering technique where only the first two partial waves have been considered (due to the smallness of the substrate reflectance, $R_{sub} \simeq 0.08$) and where the interference contributions between such partial waves have been neglected (since the coherence length of the radiation source ($\sim 1\,\mu$m) is much smaller than the substrate thickness ($=1$ mm)). Using the measured data $R_{sub} \simeq 0.08$ and $T_{sub} = 0.86$ together with the well-known expressions for T_l and R_l, we have retrieved the effective complex dielectric permittivity of the laminate by suitably minimizing the discrepancy between the values of T and R as numerically evaluated from the above relations and their measured values reported in Fig. 1. In Figs. 2(a) and 2(b), we report the retrieved real and imaginary parts of the dielectric permittivities of the samples with $N=3$, 4, 5 bilayers without optical pumping and in Fig. 2(a), we also plot the theoretical $\mathrm{Re}(\epsilon_\parallel)$ from Eq. (1) and $\mathrm{Re}(\epsilon_\parallel^{(0)})$. By inspecting the figure, it is evident that the permittivity of the sample with $N=3$ bilayers largely departs from the permittivities of the samples with $N=4$ and $N=5$ bilayers. The curves relative to these last two cases are almost overlapped, agreeing better for longer wavelengths. It is then reasonable to conclude that the sample with $N=5$ bilayers can be regarded as a homogeneous medium. Additionally, from the same figure, it appears that the standard effective medium theory (dashed line) completely fails to describe the dielectric response of the nano-laminates (as expected), whereas the improved theory of Eq. (1) (solid line) provides an accurate description. Figure 2(c) is a magnified copy of Fig. 2(a) in the spectral range $580\,\mathrm{nm} < \lambda < 610\,\mathrm{nm}$, where $\mathrm{Re}(\epsilon_\parallel)$ changes sign, as predicted by the model and confirming the validity of our approximation. The same retrieval procedure was repeated for the R and T data acquired in the presence of the optical pumping (reported in panels (d) and (e) of Fig. 1). The result is reported in Fig. 3. By comparing Fig. 3(b) with Fig. 2(b), we note that the imaginary part of the permittivity globally decreases over the spectral range where the dye molecules are active (the emission spectrum of the dye is reported in Fig. 3(d), in arbitrary units). Additionally, a close

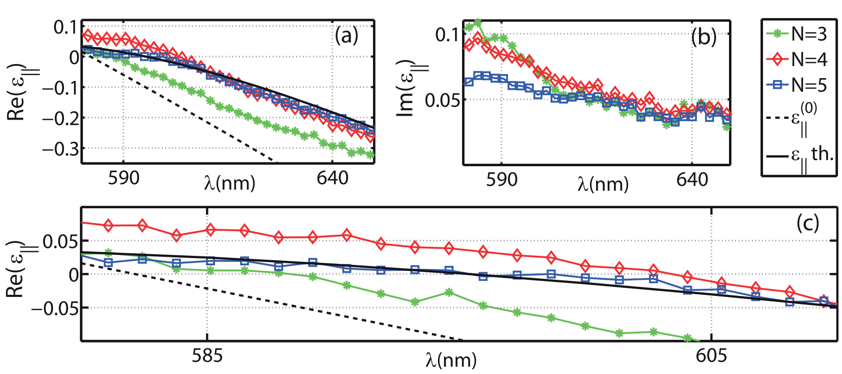

FIG. 2. (Color online) Retrieved dielectric permittivity $\epsilon_\parallel$ of the samples, without optical pumping, made up of $N=3$, 4, 5 metallo-dielectric bilayers (solid lines with markers) as a function of the vacuum wavelength λ. In panel (a), $\mathrm{Re}(\epsilon_\parallel)$ is plotted together with theoretical $\mathrm{Re}(\epsilon_\parallel)$ evaluated from Eq. (1) (solid lines without markers) and $\mathrm{Re}(\epsilon_\parallel^{(0)})$ obtained from the standard effective medium theory (dashed line). In panel (b), $\mathrm{Im}(\epsilon_\parallel)$ is reported, whereas panel (c) is a magnified copy of panel (a) in the spectral range $580\,\mathrm{nm} < \lambda < 610\,\mathrm{nm}$ within which $\mathrm{Re}(\epsilon_\parallel)$ changes sign.

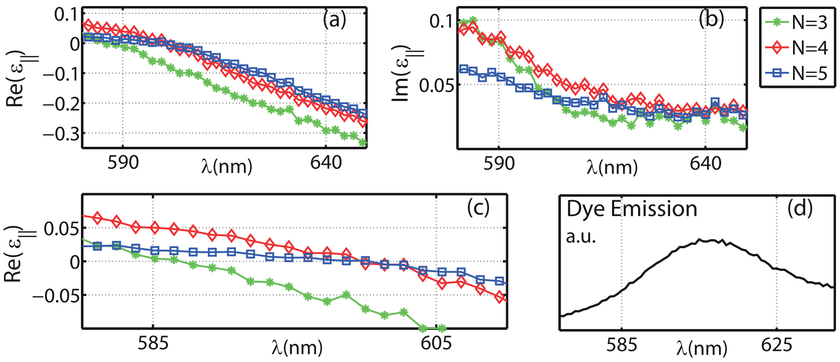

FIG. 3. (Color online) Retrieved dielectric permittivity $\epsilon_\parallel$ of optically pumped samples made up of $N = 3$, 4, 5 metallo-dielectric bilayers, as a function of the vacuum wavelength λ. (a) $\mathrm{Re}(\epsilon_\parallel)$; (b) $\mathrm{Im}(\epsilon_\parallel)$; (c) magnified copy of panel (a) in the spectral range $580\,\mathrm{nm} < \lambda < 610\,\mathrm{nm}$; (d) dye molecules emission spectrum (arbitrary units).

analysis of Fig. 3(a) shows that the optical gain has a limited effect on the real part of the effective permittivity of the samples. In particular, in the presence of optical pumping, from Fig. 3(c) and for the sample with $N = 5$, we note that the wavelength at which $\mathrm{Re}(\epsilon_\parallel)$ vanishes is shifted to $\lambda = 599\,\mathrm{nm}$. This shift confirms the validity of Eq. (1), which correctly predicts the mixing of the real and imaginary parts of the permittivity.

This result manifestly shows that the minimization of the real part of the permittivity (ENZ condition) can be achieved together with the reduction of its imaginary part, thus yielding an overall decrease of the absolute value of the sample effective permittivity. In Fig. 4, we plot the absolute value of the permittivity of the sample with $N = 5$ bilayers, both with and without optical pumping. The overall decrease of $|\epsilon_\parallel|$ is particularly evident. In particular, we obtain that, for the optically pumped sample, $|\epsilon_\parallel|$ attains its minimum value 0.04 at $\lambda = 604\,\mathrm{nm}$, which corresponds to a 21.5% decrease of the minimum $|\epsilon_\parallel| = 0.051$ (at $\lambda = 606\,\mathrm{nm}$) obtained without optical pumping. Note that the minimum of $|\epsilon_\parallel|$ is not exactly attained at the wavelength where $\mathrm{Re}(\epsilon_\parallel) \simeq 0$ (i.e., at $\lambda = 599\,\mathrm{nm}$) and this is a consequence of the fact that the emission spectrum of the dye molecules has its maximum at $\lambda = 610\,\mathrm{nm}$ (see Fig. 3(d)).

In conclusion, we have experimentally investigated the homogenization of a nano-laminate with metal and dielectric gain constituents, with layers' thickness beyond the limit of validity of the standard effective medium theory. On the other hand, we have shown that the permittivity is correctly described by an improved approach, which has allowed us to tailor the geometry to achieve the ENZ condition at a visible wavelength. In the presence of optical pumping, we have shown that the imaginary part of the permittivity can be decreased, thus proving that the generalized ENZ where the absolute value of the permittivity is very small can actually be observed. We predict that our results can open different ways to achieve efficient optical steering based on the generalized ENZ condition $|\epsilon| \ll 1$.

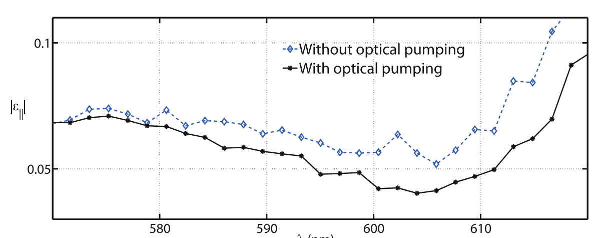

FIG. 4. (Color online) Absolute value of the permittivity of the sample with $N = 5$ metal/polymer bilayers both with and without optical pumping.

We thank Salvatore Gambino for assistance with the choice of the dye and its characterization. A.D.F. is supported by an EPSRC Career Acceleration Fellowship (EP/I004602/1). C.R. is supported by "Futuro in Ricerca" FIRB–grant PHOCOS–RBFR08E7VA.

[1]M. G. Silveirinha and N. Engheta, Phys. Rev. Lett. **97**, 157403 (2006).
[2]A. Alu, M. G. Silveirinha, A. Salandrino, and N. Engheta, Phys. Rev. B **75**, 155410 (2007).
[3]V. C. Nguyen, L. Chen, and K. Halterman, Phys. Rev. Lett. **105**, 233908 (2010).
[4]S. Feng and K. Halterman, Phys. Rev. Lett. **100**, 063901 (2008).
[5]A. Ciattoni, C. Rizza, and E. Palange, Opt. Lett. **35**, 2130 (2010).
[6]A. Ciattoni, C. Rizza, and E. Palange, Phys. Rev. A **83**, 043813 (2011).
[7]C. Rizza, A. Ciattoni, and E. Palange, Phys. Rev. A **83**, 053805 (2011).
[8]J. Karri and A. R. Mickelson, "Silver dielectric stack with near-zero epsilon at a visible wavelength," in 2009 IEEE Nanotechnology Materials and Devices Conference, Traverse City, Michigan, 2–5 June (IEEE, New York, 2009).
[9]M. J. Roberts, S. Feng, M. Moran, and L. Johnson, J. Nanophotonics **4**, 043511 (2010).
[10]W. Chen, K. P. Chen, M. D. Thoreson, A. V. Kildishev, and V. M. Shalaev, Appl. Phys. Lett. **97**, 211107 (2010).
[11]J. Elser, V. A. Podolskiya, I. Salakhutdinov, and I. Avrutsky, Appl. Phys. Lett. **90**, 191109 (2007).
[12]R. J. Pollard, A. Murphy, W. R. Hendren, P. R. Evans, R. Atkinson, G. A. Wurtz, and A. Zayats, Phys. Rev. Lett. **102**, 127405 (2009).
[13]A. Ciattoni, C. Rizza, and E. Palange, Phys. Rev. A **81**, 043839 (2010).
[14]T. A. Klar, A. V. Kildishev, V. P. Drachev, and V. M. Shalaev, IEEE J. Sel. Top. Quantum Electron. **12**, 1106 (2006).
[15]S. Wuestner, A. Pusch, K. L. Tsakmakidis, J. M. Hamm, and O. Hess, Phys. Rev. Lett. **105**, 127401 (2010).
[16]S. Xiao, V. P. Drachev, A. V. Kildishev, X. Ni, U. K. Chettiar, H. K. Yuan, and V. M. Shalaev, Nature **466**, 735 (2010).
[17]A. Bratkovsky, E. Ponizovskaya, S. Wang, P. Holmstrom, L. Thylen, Y. Fu, and H. Agren, Appl. Phys. Lett. **93**, 193106 (2008).
[18]Z. G. Dong, H. Liu, T. Li, Z. H. Zhu, S. M. Wang, J. X. Cao, S. N. Zhu, and X. Zhang, Appl. Phys. Lett. **96**, 044104 (2010).
[19]Y. Fu, L. Thylen, and H. Agren, Nano Lett. **8**, 1551 (2008).
[20]P. Holmstrom, L. Thylen, and A. Bratkovsky, Appl. Phys. Lett. **97**, 073110 (2010).
[21]K. J. Webb and A. Ludwig, Phys. Rev. B **78**, 153303 (2008).
[22]I. D. Leon and P. Berini, Opt. Express **17**, 20191 (2009).
[23]I. D. Leon and P. Berini, Nature Photon. **4**, 382 (2010).
[24]M. A. Noginov, V. A. Podolskiy, G. Zhu, M. Mayy, M. Bahoura, J. A. Adegoke, B. A. Ritzo, and K. Reynolds, Opt. Express **16**, 1385 (2008).
[25]M. A. Noginov, G. Zhu, M. Mayy, B. A. Ritzo, N. Noginova, and V. A. Podolskiy, Phys. Rev. Lett. **101**, 226806 (2008).
[26]A. D. Rakic, A. B. Djuriic, J. M. Elazar, and M. L. Majewski, Appl. Opt. **37**, 5271 (1998).
[27]The value $\mathrm{Re}(\epsilon_{PMMA}) = 1.95$ is slightly different from the standard value $\epsilon_{PMMA} = 2.22$ in order to consider the effect of the dye molecules. Besides, we neglected $\mathrm{Im}(\epsilon_{PMMA})$ in the tailoring of the structure.