On the dielectric function tuning of random metal-dielectric nanocomposites for metamaterial applications

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Abstract: The potential of random metal-dielectric nanocomposites as constituent elements of metamaterial structures is explored. Classical effective medium theories indicate that these composites can provide a tunable negative dielectric function with small absorption losses. However, the tuning potential of real random composites is significantly lower than the one predicted by classical theories, due to the underestimation of the spectral range where topological resonances take place. This result suggests that a random mixture consisting of a metal matrix with embedded isolated dielectric inclusions is a promising design guideline for the fabrication of tunable composites for metamaterial purposes.

OCIS codes: (310.6860) Thin films, optical properties; (240.6680) Surface plasmons; (160.3918) Metamaterials.

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1. Introduction

Research on metamaterial structures undergoes continuous progress due to their unique electromagnetic behavior and the associated application potential [1]. With constant advances in design approaches [2] and fabrication capabilities [3], metamaterial development appears to be restricted by the properties of naturally available materials used to build metamaterial structures. For instance, the near field superlens slab can provide perfect focusing of light in the near field region if the lens material has negligible absorption losses and its dielectric function equals to $-\varepsilon_H$, where ε_H is the dielectric function of the host surrounding the slab [4]. Such characteristics are best matched by metals, particularly silver [5,6], but only in a reduced spectral range, including the near ultraviolet and part of the visible. Alternatively, polar crystals like SiC can provide superlensing in the mid-infrared range [5]. A wider operational range of superlenses could have a strong potential application in areas like near field spectroscopy, lithography or microscopy [1,6]. Overall, materials with negative dielectric function in the optical range are essential for many metamaterial designs and the choice is usually limited to noble metals [7].

An interesting route to obtain materials with tailorable dielectric function is the use of metal-dielectric mixtures. In particular, random metal dielectric composites are easy to prepare using thin film deposition techniques and their effective dielectric function can be varied by controlling the mixture composition. It has been suggested to use such composites to tune the operational wavelength of a superlens slab in a broad spectral range by just adjusting the metal filling factor [8]. Further tuning was later proposed by modifying also the particle shape in the composite [9]. The performance of metal-dielectric multilayer sub-wavelength imaging structures can be improved when replacing the metal layers by metal-dielectric composites [10,11]. The potential benefits of metal-dielectric mixtures are not restricted to the near-field superlens only. These composites may enable wavelength-tuning of super-resolution devices operating in the far field [12], improve the performance of negative index structures [13,14] cloaking devices [15] and provide transparency or extreme anisotropy [16].

In most of the mentioned works [8–15], the effective dielectric function of the metal-dielectric composite was assumed to follow the Bruggeman mixing formula [17]. Recently, it has been pointed out that a composite whose effective dielectric function is described by the Maxwell-Garnett [18] formalism can also show negative dielectric function [16,19]. In any case, effective medium theories describe the effective dielectric function of complex systems through the dielectric function of the components and a limited number of parameters, usually the filling fraction of the components only [20]. Therefore, these theories can provide just an approximate description of the effective behavior of complex mixtures and it is questionable to what extent real random metal-dielectric composites can be described by simple mixing formulae. For example, numerical simulations based on the finite difference time domain method showed that random composites have significant absorption in a spectral range broader than the one predicted by the Bruggeman theory, highly undesirable for most metameterial requirements [21]. In addition to the theoretical work, there have been some recent attempts to fabricate metal-dielectric composites for superlens purposes [22,23]. Indeed, the obtained composites show unwanted absorption significantly higher than the one predicted by effective medium theory, acknowledging that a more advanced description is necessary for a correct prediction of the observed effective dielectric function.

In the present work we analyze the potential and limitations of random metal-dielectric composites for metamaterial applications. First, the classical effective medium theories of

Maxwell-Garnett and Bruggeman are re-visited in the framework of the Bergman spectral density representation. It is shown that both of these theories can lead to a negative effective dielectric function based on different physical mechanisms: surface plasmon resonance of isolated metal particles and percolation of the metal component. Next, the limitations of these effective medium theories are analyzed by characterization of different fabricated random metal-dielectric composites. Although these theories explain the behavior of the composites qualitatively, they significantly underestimate absorption at wavelengths where tuning is sought. The determination of the spectral density function of these composites from experimental measurements evidences that the unwanted absorption is closely related to the random nature of the composites. Finally, in the last section, a random composite topology consisting of metal matrix with embedded isolated dielectric inclusions, is proposed. It is shown that the potential of such composite for metamaterial purposes is almost unaffected by the random nature of the mixture.

2. Effective medium theories and spectral density representation

Effective medium theories define an effective dielectric function for a composite material in terms of the dielectric function of its components and their geometrical arrangement [20,24]. The applicability of effective medium theories is restricted by the size of the structures composing the mixture: sufficiently large to preserve locally their own electromagnetic behavior and small enough for the composite to appear homogeneous compared to the wavelength of the interacting radiation. Over the last century numerous effective medium theories have been proposed, being the Maxwell-Garnett and the Bruggeman expressions the most successful to explain the effective behavior of a large number of composites. If the mixture consists of isolated and poorly interacting spherical metal inclusions embedded in a dielectric matrix, the Maxwell-Garnett formula reads as:

$$\frac{\varepsilon_{eff}-\varepsilon_1}{\varepsilon_{eff}+2\varepsilon_1}=p\frac{\varepsilon_2-\varepsilon_1}{\varepsilon_2+2\varepsilon_1}, \quad (1)$$

where ε_{eff} is the effective dielectric function, ε_1 is the dielectric function of the matrix, ε_2 is the dielectric function of the metal inclusions and p is the filling fraction of metal in the composite. Another commonly found topology corresponds to aggregate systems with some degree of interconnection between the two components. The role of matrix and inclusions cannot be clearly defined and the matrix where the phases are mixed is considered to be the effective medium itself. For these cases, the Bruggeman theory appears to be more appropriate:

$$p\frac{\varepsilon_2-\varepsilon_{eff}}{\varepsilon_2+2\varepsilon_{eff}}+\left(1-p\right)\frac{\varepsilon_1-\varepsilon_{eff}}{\varepsilon_1+2\varepsilon_{eff}}=0. \quad (2)$$

Metal-dielectric composites with effective dielectric function that obeys the previous expressions can show a negative real part of the effective dielectric function ($\mathrm{Re}(\varepsilon_{eff}) < 0$) which absolute value can be adjusted by controlling the filling fraction [8,19]. However, from the above expressions it is not evident by which physical mechanism $\mathrm{Re}(\varepsilon_{eff}) < 0$ is obtained. A more general description of the geometry-related features that are contained in each effective medium theory can be obtained in the context of the spectral density theory [25]. This theory states that any effective dielectric function of a composite made of two components with dielectric functions ε_1 and ε_2 can be expressed as [26,27]:

$$\varepsilon_{eff}=\varepsilon_1\left(1-p\int_0^1\frac{g\left(u,p\right)}{t-u}du\right), \quad (3)$$

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where u is an integral variable, $t = \varepsilon_1 /(\varepsilon_1 - \varepsilon_2)$ and $g(u, p)$ is the spectral density function. The above expression, known also as Bergman representation, presents the effective dielectric function as a sum of poles that can be identified with resonances related to the topology of the system. These resonances take place for values of the parameter t between 0 and 1 and have a weight given by $g(u, p)$. The spectral density function depends uniquely on the geometrical arrangement of the components in the mixture. Therefore, the Bergman representation explicitly separates the effects of the composite topology, enclosed in $g(u, p)$, and of the specific dielectric functions of the composing materials, contained in t. It appears that the closer the values of t to the real interval [0, 1], the stronger the influence of the composite topology on the effective dielectric function. This is actually the case of many metal-dielectric composites as shown in Fig. 1 for SiO_2-Ag and SiC-Ag mixtures with optical constants taken from literature [28,29].

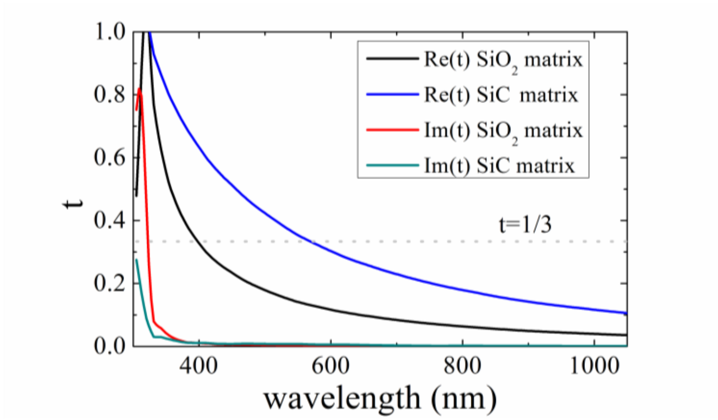

Fig. 1. Real and imaginary part of parameter $t = \varepsilon_1/(\varepsilon_1 - \varepsilon_2)$ for SiO_2-Ag and SiC-Ag mixtures.

The spectral density function $g(u, p)$ can be split in two contributions [26]: a delta-function at $u = 0$, that represents the percolation among inclusions and a continuous part (g_{cont}) that accounts for the interaction of isolated inclusions among themselves and with the matrix. Thus, the effective dielectric function can be expressed as:

$$\varepsilon_{eff} = pg_o(p)\varepsilon_2 + (1 - pg_o(p))\varepsilon_1 - \varepsilon_1 p\int_0^1 \frac{g_{cont}(u, p)}{t - u} du, \tag{4}$$

with g_o being the percolation strength that quantifies the degree of interconnectivity among inclusions. Therefore, the percolation of inclusions contributes to the effective dielectric function with a weighted average of the dielectric functions of the composing materials.

The spectral density function of the Maxwell-Garnett theory is a delta function [30]:

$$g_{MG}(u, p) = \delta\left(u - \frac{1-p}{3}\right). \tag{5}$$

Thus, the Maxwell-Garnett theory predicts a single resonance for $t = (1- p)/3$, that in the dilute limit ($p \to 0$) corresponds to the surface plasmon resonance of isolated spherical particles in the quasi-static approximation ($\varepsilon_2 = - 2\varepsilon_1$) [31]. Combining Eqs. (5) and (3) it appears that a negative real part of the effective dielectric function can be achieved if the parameter t is between $(1- p)/3$ and $(1 + 2p)/3$. Thus, the condition $\mathrm{Re}(\varepsilon_{eff}) < 0$ is obtained for wavelengths below the resonance and the range of wavelengths where $\mathrm{Re}(\varepsilon_{eff}) < 0$ can be obtained is wider as p increases. Figure 2 shows the dependence of the effective dielectric function on the wavelength and filling fraction for composites consisting of Ag inclusions in either SiO_2 or SiC matrix with optical constants taken from literature [28,29] . The dashed lines in Fig. 2

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correspond to Re(ε_{eff}) = – Re(ε_{SiC}), i.e. with the composite matching a SiC host in a near-field superlens structure (matching condition) [8].

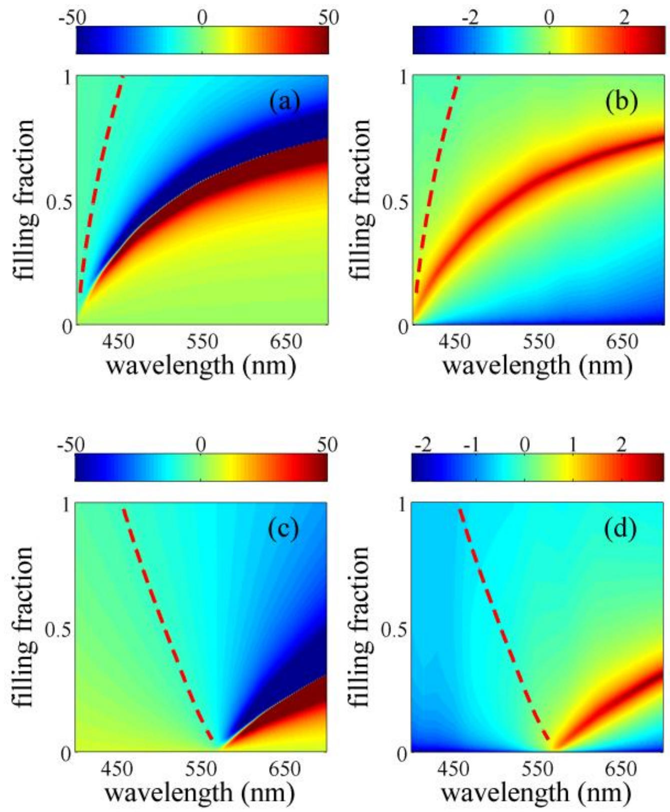

Fig. 2. Effective dielectric function of a dielectric–Ag composite computed with the Maxwell-Garnett formula: (a, c) real part, (b, d) logarithm of imaginary part. The dielectric matrix is SiO_2 (a, b) and SiC (c, d). The dashed line corresponds to the matching condition for the composite operating as a near-field superlens in a SiC host.

For the Bruggeman effective medium theory, the spectral density function reads as [30]:

$$g_{BG}(u,p)=\frac{3p-1}{2p}\delta^{+}(u)\theta(3p-1)+\frac{3}{4\pi pu}\sqrt{(u-u_L)(u_R-u)}\theta(u-u_L)\theta(u_R-u), \quad (6)$$

with

$$u_{R/L}=\frac{1}{3}\left(1+p\pm2\sqrt{\left(2p-2p^2\right)}\right), \quad (7)$$

and θ is the Heaviside step function. The first term describes the percolation of metal component that increases with p and is zero below the percolation threshold (p_c = 1/3). The second term is a continuous distribution of resonances between u_L and u_R and accounts for the interaction among inclusions. Figure 3 shows the effective dielectric function of a SiO_2–Ag composite computed with the Bruggeman formula. At low filling fraction there is a single surface plasmon resonance that rapidly broadens and red-shifts as p increases. On the contrary to the Maxwell-Garnett theory, the resonance is not strong enough to lead to negative values of the effective dielectric function. As p increases above the percolation threshold, the surface plasmon resonance vanishes and the effective dielectric function is dominated by the

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percolation contribution. Thus, negative values of the dielectric function are obtained for p well above p_c by simple averaging the dielectric functions of the components.

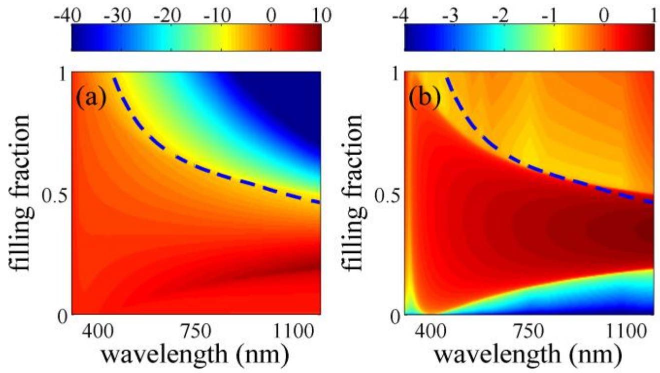

Fig. 3. Effective dielectric function of a SiO_2–Ag composite computed with the Bruggeman formula: (a) real part, (b) logarithm of imaginary part. The dashed line corresponds to the matching condition for the composite operating as a near-field superlens in a SiC host.

The effective dielectric function at $p = 2/3$ for different composites is shown in Fig. 4(a) in order to illustrate that negative values of the effective dielectric function are obtained based on different phenomena for each effective medium theory. In addition to the condition $Re(\varepsilon_{eff}) < 0$, negligible absorption losses are also required for practical issues. Thus, most material quality factors for metamaterial and plasmonic applications involve the ratio between the real and imaginary part of the dielectric function [7]. For instance, for the near-field superlens, the quality factor defined as:

$$QF = -\frac{\ln\left(\frac{Im(\varepsilon_{eff})}{2Re(\varepsilon_{eff})}\right)}{2\pi}, \tag{8}$$

quantifies the resolution power of the superlens slab. Figure 4(b) shows the quality factor for dielectric-Ag composites matching a SiC host. At 451 nm the quality factor is maximum, coinciding with the case of pure silver (i.e. $p = 1$). Although it is possible to tune the wavelength where the matching condition takes place using both theories, the Maxwell Garnett theory offers tuning in a rather limited spectral range. The quality factor rapidly decreases as p reduces. Additionally, it is difficult to obtain a real system of isolated particles with p close to 1 and no percolation, as required by the Maxwell-Garnett description. On the contrary, the Bruggeman theory enables tuning in a much broader spectral range with a quality factor comparable to that of pure Ag. The quality factor starts to decrease at large wavelengths only, where imaginary part of the dielectric function is affected by the absorption related to the surface plasmon resonance, as shown in Fig. 4(b). Therefore, the wider wavelength tuning range and higher quality factor obtained using the Bruggeman effective medium theory indicates that tuning based on percolation of the metal component can offer better performance than tuning based on the surface plasmon resonance of isolated particles. It must be remarked that optical constants of bulk Ag are considered in these simulations. If the nanocomposite contains very small metal particles, typically below 5-10 nm, size confinement effects can appear [32], resulting in a larger imaginary part of the dielectric function of Ag that would worsen the composite performance.

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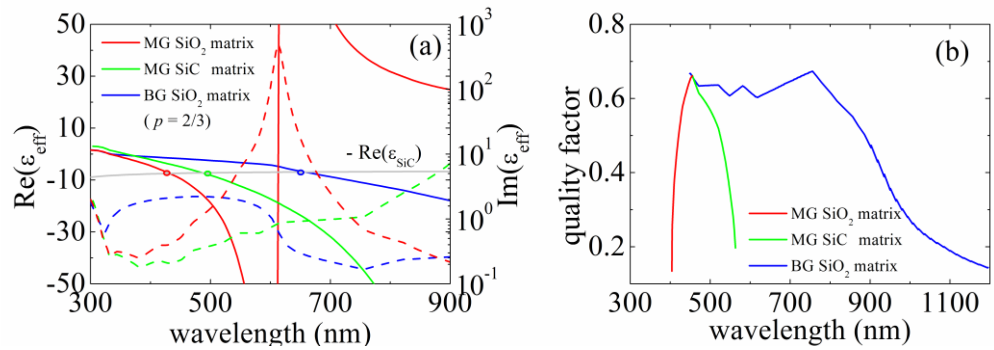

Fig. 4. (a) Real (solid) and imaginary (dashed) part of the effective dielectric function of dielectric-Ag composites using the Maxwell-Garnett and Bruggeman theories. (b) Quality factor Eq. (8) for a dielectric-Ag composite superlens matching a SiC host. In both figures the composites are: SiO_2–Ag using the Maxwell-Garnett theory (red), SiC–Ag using the Maxwell-Garnett theory (green), and SiO_2–Ag using the Bruggeman theory (blue).

3. Fabrication and characterization of random metal-dielectric composites

In order to analyze to what extent the prediction of effective medium theories agree with the real behavior of random metal-dielectric composites, a set of SiO_2-Ag layers was fabricated and characterized. The composite layers were obtained by the subsequent deposition of SiO_2, Ag and SiO_2 on a glass substrate. SiO_2 layers were 80 nm thick and Ag layer mass thickness was up to 15 nm. Due to the small amount of deposited metal, an island-like growth takes place resulting in the formation of metal nanoclusters rather than a compact Ag film [33]. The depositions were performed by electron beam evaporation in a modified Varian chamber with a base pressure of 10^{-7} torr, using quartz crystal to monitor the deposited nominal mass thickness. The deposition rates of Ag and SiO_2 were ~0.1 and 1 nm/s respectively. The island-like growth of Ag depends on the deposition temperature [34,35]. Thus, according to our previous studies of metal clusters obtained with the above mentioned system [36], two series of samples were produced: one using substrates heated at 220 °C prior and during the deposition and the other set without pre-heating. The island formation is enhanced on pre-heated substrates, resulting in more spherical and larger particles than for samples deposited onto unheated substrates, where irregular shapes are obtained and percolation among islands is achieved with a smaller amount of deposited metal [33,36]. Thus, the set of samples deposited onto pre-heated substrates is expected to have a topology close to the assumptions of the Maxwell-Garnett theory, while the samples deposited onto unheated substrates should fit better into the Bruggeman description. For each set, samples with different Ag mass thickness were produced. It must be remarked that the aim of this experimental study is to analyze the discrepancies between the predictions of effective medium theories and the behavior of real random composites and not to fabricate a composite for a given metamaterial application. Thus, neither the total thickness of the composite nor its surface roughness was optimized for a favorable performance [22,23].

Optical measurements allowed retrieving the effective dielectric function and thickness of the composite layer, modeled as sketched in Fig. 5. The measurements were performed in the spectral range between 275 and 2000 nm with a J. A. Woollam V-VASE ellipsometer. Ellipsometric data were taken at angles of incidence 45°, 55°, and 65° and transmittance spectra were taken at normal incidence. This combination of measurements was used as it enables a precise simultaneous determination of the dielectric function and thickness of very thin absorbing films [37]. The dielectric function of the composite was modeled using a multiple-oscillator approach that takes into account both the surface plasmon resonance of isolated particles and the percolation effects [38,39]. For all the analyzed samples it was possible to obtain very satisfactory data fits (Fig. 6).

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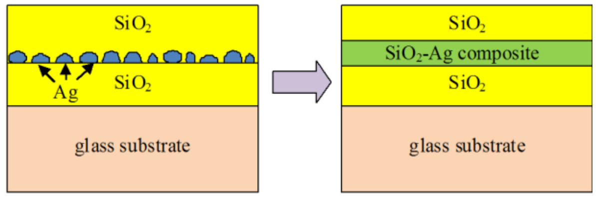

Fig. 5. Sketch of the fabricated samples (left) and model for extraction of effective dielectric function and thickness of the Ag-SiO_2 composite from optical measurements (right).

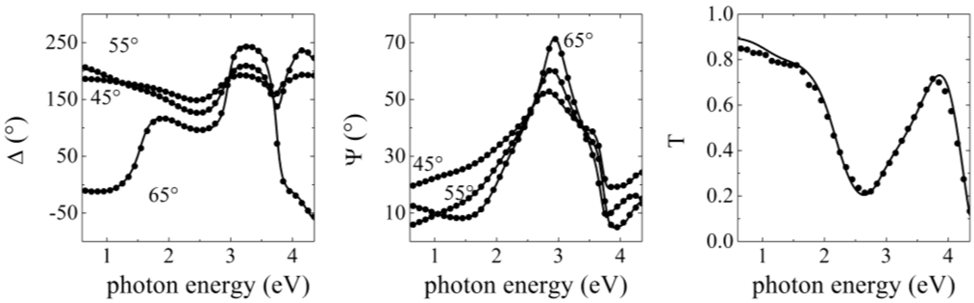

Fig. 6. Experimental ellipsometry and transmittance measurements (symbols) and model simulation (solid lines) for a SiO_2-Ag composite with nominal Ag mass thickness of 8 nm deposited onto a pre-heated substrate.

3.1 Composites deposited onto pre-heated substrates

The effective dielectric constant of SiO_2-Ag composites deposited onto pre-heated substrates is shown in Fig. 7(a) and Fig. 7(b). The filling fraction of the composite, estimated as the ratio between the deposited mass thickness and the effective thickness obtained by fitting of optical measurements, varies between 0.15 and 0.45. Qualitatively, the observed behavior agrees well with the Maxwell-Garnett theory: the wavelength-dependence of the effective dielectric function is dominated by the surface plasmon resonance of metal nanoparticles, that red-shifts and broadens as the metal filling fraction increases. However, the range where $\mathrm{Re}(\varepsilon_{eff}) < 0$ is markedly shorter than the one predicted by the Maxwell-Garnett theory [Eq. (1)] or by its two-dimensional counterpart [16]. In addition, the imaginary part of the effective dielectric function far from the surface plasmon resonance peak shows values higher than the predicted by the theory. Thus, the quality factor of the fabricated composites is significantly smaller than for SiO_2-Ag Maxwell-Garnet composites.

The differences between the Maxwell-Garnett theory prediction and the deposited composites are related to a surface plasmon resonance broader than the computed one. Our previous studies of similar composites indicate that the minimum typical particle size is approximately 10 nm [36] and consequently the broadening cannot be related to confinement effects [32]. Thus, the experimentally determined broader surface plasmon resonance appears to be associated to the inappropriateness of the Maxwell-Garnett theory for these composites. In order to analyze this discrepancy, the spectral density function has been inverted numerically from the experimentally determined effective dielectric function, in a similar way to the one presented in [40,41]. Basically, the procedure consists in the discretization of the spectral density function at N (N = 100) equidistant points located in the range [0,1] of the integral variable u. The values of the spectral density at each point are found by non-linear constrained optimization. The function to minimize is the difference between the experimentally determined effective dielectric function and the dielectric function computed using Eq. (3) with t calculated from the dielectric functions of Ag and SiO_2. In addition, regularization conditions are imposed to preserve the mathematical properties of the spectral density function [26]: non-negativity and sum rules related to the zeroth and first order

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moments. Fitting of the experimentally determined effective dielectric function was satisfactory for all the samples (solid lines in Fig. 7). When the filling fraction was included as unknown parameter in the inversion process, the obtained value was very close (up to ± 5%) to the ratio between the nominal mass thickness and the effective thickness found by optical characterization.

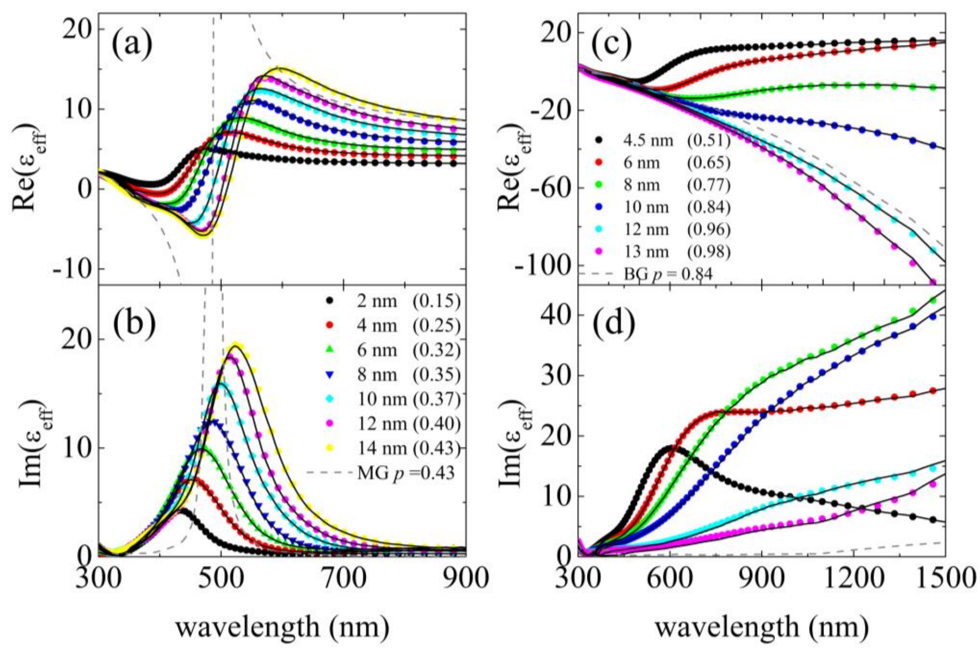

Fig. 7. Real (a, c) and imaginary (b, d) part of the effective dielectric function of SiO_2-Ag composites with different Ag mass thickness (indicated in nm) deposited onto pre-heated (a, b) and unheated (c, d) substrates. The number in brackets is the ratio between nominal thickness and effective thickness obtained by ellipsometry. Solid lines are best-fits obtained by numerical inversion of the spectral density function. Effective dielectric functions of SiO_2-Ag composites computed using the Maxwell-Garnett (a, b) and Bruggeman (c, d) theories at two different filling fractions are shown (gray dashed line) for comparison.

The obtained spectral density functions are shown in Fig. 8(a). In all cases, the spectral density function consists of a broad peak instead of a delta peak, what can be related to the local field fluctuations characteristic for a random system. In a disordered system, each inclusion will have its own surface plasmon resonance condition, strongly affected by the interaction with neighbor particles. Consequently, resonances appear for a wide range of t values, finally resulting in a broad surface plasmon resonance. Indeed, the obtained results are in good qualitative agreement with the spectral density function of a system of randomly located polarizable spheres as calculated numerically [42]. The broadening of the spectral density cannot be exclusively associated to the spatial disorder of the inclusions. It has been shown that inclusions with a shape distribution lead to a broadened distribution of resonances since the local field acting on each particle also depends on the particle shape [34,43]. In any case, the randomness of the composite topology results in a broad surface plasmon resonance that increases absorption and reduces the range with $Re(\varepsilon_{eff}) < 0$, dramatically reducing the composite potential for metamaterial purposes.

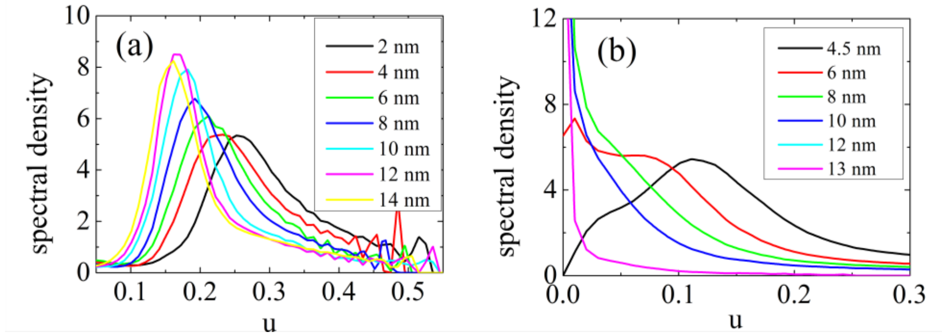

Fig. 8. Spectral density function of SiO_2-Ag composites deposited onto pre-heated (a) and unheated (b) substrates obtained by numerical inversion of the effective dielectric function.

3.2 Composites deposited onto unheated substrates

The effective dielectric functions of the SiO_2-Ag composites deposited onto unheated substrates are shown in Fig. 7(c) and Fig. 7(d). The filling fractions of the composites, calculated as the ratio between the deposited mass thickness and the effective thickness obtained by optical characterization, are larger (p ~0.5 - 1) than those for composites deposited onto pre-heated substrates. Qualitatively, the behavior of the effective dielectric function fits into the Bruggeman description: composites with low metal filling fraction present significantly broader surface plasmon resonance than composites deposited onto pre-heated substrates. As the filling fraction increases, the contribution of the surface plasmon resonance vanishes and the effective dielectric function becomes closer to a weighted average of the dielectric functions of pure Ag and SiO_2. This indicates that the percolation of metal inclusions dominates the observed optical behavior. Thus, it is possible to tune widely $Re(\varepsilon_{eff}) < 0$ for high metal filling fractions, as predicted by the Bruggeman theory. However, a quantitative comparison indicates that the absorption is higher than the one computed by the theory, even in the spectral range unaffected by the surface plasmon resonance. This larger absorption, that has been also observed in recent numerical [21] and experimental studies [22,23], results in less optimal characteristics for applications. Thus, while the Bruggeman theory predicts quality factors comparable to the one of pure Ag (~0.65) when the matching condition wavelength is not affected by the surface plasmon absorption (Fig. 4), the fabricated composites have quality factors between 0.2 and 0.4.

Same as for the composites deposited on pre-heated substrates, the spectral density function has been extracted numerically from the experimentally determined effective dielectric function. In addition to the discretization of the spectral density, the percolation strength is also included as an unknown parameter in the optimization process. The resulting spectral density function is shown in Fig. 8(b). The percolation threshold appears to be for values of p between 0.65 and 0.77 and the percolation strength, g_o, grows monotonically for larger p. The continuous part of the spectral density function consists of a peak that broadens and shifts to lower u as the filling fraction approaches the percolation threshold. This trend is qualitatively similar to the behavior of the Bruggeman theory. Above the percolation threshold, the spectral density function extends through the whole range [0, 1], rapidly decaying with u. It has been shown previously that percolated metal-dielectric random composites fabricated by evaporation process present typically a fractal structure consisting of metal inclusions of all sizes, ranging from isolated clusters to a large connected metal network [1,20]. Therefore, every topological resonance can take place in such system, leading to absorption in broad electromagnetic spectrum. The presence of a continuous distribution of all possible resonances for filling fractions above the percolation threshold has been also experimentally observed in other random systems, such as metal-polymer composites [44],

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porous silicon [45] or ultra-rough silver films [46]. Regarding the effective dielectric function, the topological resonances will result in additional absorption when the values of *t* are close to zero. According to Fig. 1, such resonances will affect directly the spectral region where the matching condition is achieved. The Bruggeman theory does not consider topological resonances for small values of *t* if the filling fraction is large enough. Hence, an ideal Bruggeman composite would have better performance from the application point of view than a real percolated system with fractal structure.

4. An alternative random metal-dielectric composite topology

The random nature of the fabricated composites decreases their performance for metamaterial purposes in respect to the predictions of effective medium theories. It appears that tuning of the effective dielectric function based on the percolation of metal is a more attractive approach than controlling the surface plasmon resonance of isolated inclusions. Improved performance of composites could be obtained if the continuous distribution of resonances is minimized, i.e. if the metal component would be percolated but not having a fractal structure. This condition can be realized by a random system consisting of isolated dielectric inclusions in a metal matrix. Such system could correspond to the composites deposited onto pre-heated substrates but with exchanged roles of the metal and dielectric components. In this case, the spectral density function of the system would be the one calculated from experimental measurements [Fig. 8(a)] and the effective dielectric function of the mixture can be calculated using Eq. (3) by simply exchanging the dielectric functions of the matrix and inclusions (Fig. 9). It can be noticed that these composites, even having a random nature, can offer a wide range of tuning of the real part of the effective dielectric function, having absorption lower than pure Ag. Thus, the matching condition for a SiC host is achieved between 495 and 610 nm for the range of filling factors of simulated mixtures and the quality factor is close to 0.65 in all the cases. Further wavelength tuning towards the infrared part of the spectra could in principle be achieved by inclusions with higher dielectric function (for instance, SiC) or increasing the filling factor of inclusions.

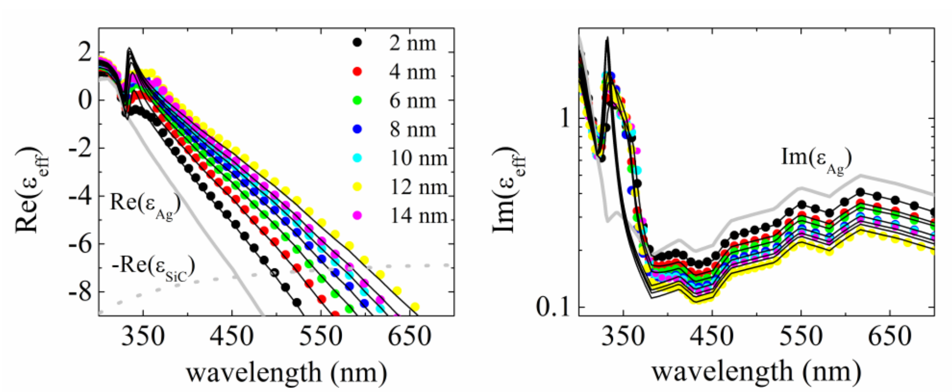

Fig. 9. Effective dielectric function of Ag-SiO_2 composite (metal matrix with dielectric inclusions) computed using the spectral densities extracted from the experimental effective dielectric function of fabricated SiO_2-Ag composites [Fig. 8(a)]. The solid lines are simulations using the Maxwell-Garnett expression.

A system consisting of dielectric inclusions in a metal matrix presents the same topological resonances as the complementary metal-in-dielectric composite. However, the resonances will now affect the values of the parameter $t' = \varepsilon_2 / (\varepsilon_2 - \varepsilon_1)$, i. e. $t' = 1 - t$. Thus, the resonances will occur around $t' = (1 - p)/3$ or, equivalently, $t = (2 + p)/3$. It means that the resonances will take place in the short-wavelength spectral range (Fig. 1) and will affect in a lesser degree the wavelengths where the condition $\mathrm{Re}(\varepsilon_{eff}) = -\mathrm{Re}(\varepsilon_{SiC})$ is achieved. The effect of the topological resonances can be observed in the imaginary part of the effective dielectric

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function around 350 nm. In the low filling fraction limit, it corresponds to the "void" plasmon resonance of a dielectric inclusion embedded in metal ($\varepsilon_2 = -\varepsilon_1/2$) [47]. This resonance does not broaden significantly as the filling fraction of dielectric inclusions increases, in opposition to the case of metal inclusions in dielectric matrix. The reason is that as the filling fraction increases, the topological resonances shift towards smaller values of t', but this affects a reduced spectral range due to the fast decrease of t' as wavelength is decreased. The spectral density functions experimentally obtained for real composites and the spectral density of the Maxwell-Garnet theory have zero or negligible values for t' corresponding to the matching condition. As a result, the effective dielectric function is very similar at the matching condition whether it is computed using the Maxwell-Garnett theory (solid lines in Fig. 9) or from the experimentally determined spectral density functions. This fact is further supported in Fig. 10, where the effective dielectric function of a composite consisting of Ag matrix and SiO_2 inclusions is calculated using the Maxwell-Garnett theory and from numerical simulations of the spectral density function of random systems of polarizable spheres as done in reference [42]. This is an important result, as it enables the use of the Maxwell-Garnett expression for computing the effective dielectric function of such composite in the spectral range where the matching condition is achieved, regardless the random nature of the mixture. Recently, it has been shown that a mixture consisting of metal matrix and dielectric inclusions and effective dielectric function described by the Maxwell-Garnett formula has superior performance for superlens purposes than the complementary composite of dielectric matrix with metal inclusions. This result was verified by numerical simulations of ordered two-dimensional void inclusions in a silver matrix [19]. The results presented here suggest that a random system could give equally good performance, what is very attractive regarding fabrication requirements.

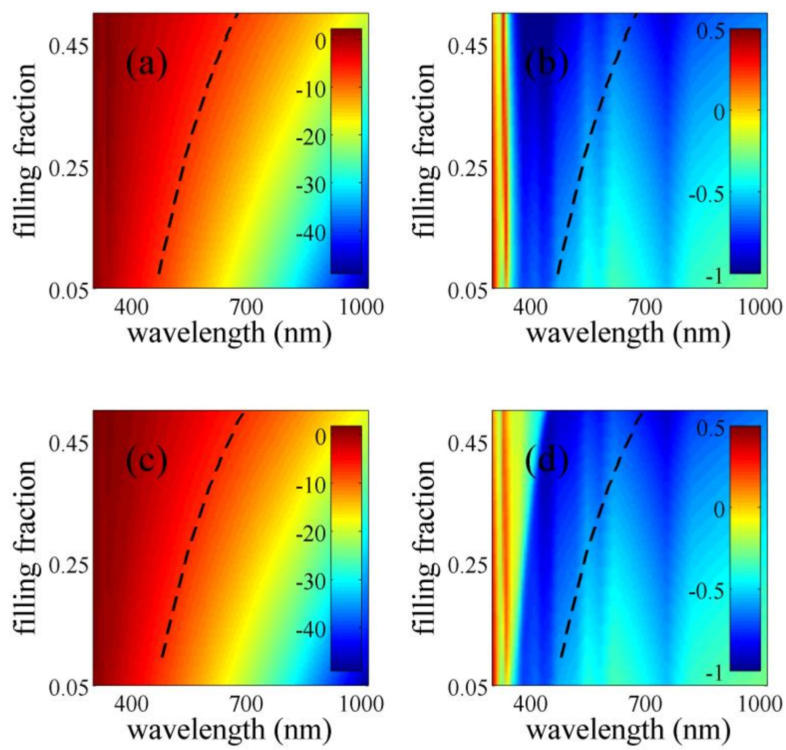

Fig. 10. Effective dielectric function of a Ag-SiO_2 composite computed with the Maxwell-Garnett formula: (a, b) and the numerically calculated spectral density for a random sytem of polarizable spheres (c, d): real part (a, c) and logarithm of imaginary part (b, d). The dashed line corresponds to the condition Re(ε_{eff}) = - Re(ε_{eff}).

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Fabrication of a composite consisting of a metal matrix with isolated dielectric inclusions by thin film deposition techniques used in this and other studies [22,23] might be complex, since the island growth is characteristic for metals and not dielectrics. Alternatively, there are several techniques for fabrication of metal films with isolated dielectric inclusions, specially voids: nanoporous gold from cluster beam deposition [48], disorder nanohole arrays from colloidal lithography [49] or nanoscale casting with electrochemical deposition [50]. Indeed, the effective dielectric function of nanoporous gold determined in reference [48] show absence of localized surface plasmon resonance in the visible range, as suggested from the above theoretical analysis.

5. Conclusions

It has been shown that a metal-dielectric composite with effective dielectric function described in the framework of classical effective medium theories can provide a negative dielectric function with small imaginary part based on the surface plasmon resonance of isolated inclusions (Maxwell-Garnett) or on the percolation of metal inclusions (Bruggeman). This observation appears from the analysis of the classical effective medium theories in the context of the spectral density representation, that explicitly states the influence of the composite geometrical configuration through the topological resonances of the system. Although both theories can lead to a negative real part of the effective dielectric function and small absorption, the Bruggeman composite presents an extended degree of wavelength tuning and improved performance.

The determination of the effective dielectric function of fabricated random metal-dielectric composites using optical spectroscopy indicates that real random systems have higher absorption than predicted by effective medium theories. These discrepancies, that limit the composite potential for metamaterial applications, appear to be closely related to the random nature of the mixtures. Thus, in systems consisting of isolated metal particles in dielectric matrix, the local field fluctuations lead to a wide range of topological resonances instead of the single resonance considered in the Maxwell-Garnett theory. This results in a surface plasmon resonance broader than the predicted by the theory, reducing the range of negative values that the real part of the effective dielectric function can take and increasing its imaginary part. The composites for which tuning of the effective dielectric function is based on percolation of the metal component, have spectral density functions consisting of a continuous distribution of all possible topological resonances, typical for fractal structures. As a result, such composites present higher absorption for the wavelength range where tuning is desired, when compared to the Bruggeman theory.

These results indicate that mixtures with the metal component being percolated, but not having a fractal nature, should present higher quality factors for metamaterial applications than the composites fabricated in this study. This is the case of a metal matrix with embedded isolated dielectric inclusions. In this mixture, the topological resonances of the system do not induce additional absorption in the spectral range where tuning is required. A metal matrix with dielectric inclusions, even randomly distributed, appears as an attractive design principle for fabrication of composites for tunable near-field superlens and for other metamaterial applications, where tailoring of the real part of the effective dielectric function is desirable, keeping at the same time a small imaginary part.

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