Adsorption-Based Reflectance Tuning of 2D Metamaterial with Ultralow Effective Refractive Index

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Abstract **— We analyzed metamaterial structures with all-positive, near-zero refractive index, composed of nanowire mesh media with a Drude-type, plasma-like dispersion of dielectric permittivity. We investigated the possibility to tune electromagnetic properties of these structures by allowing adsorption of a thin gaseous or liquid dielectric layer (down to a monomolecular or monoatomic thickness) on the wire surface, or, alternatively, by immersing the structure into fluid. We calculated spectral reflection of our structures and determined the dependence of the reflectance dip frequency on the thickness and the refractive index of the adsorbed dielectric material layer. Our results could be useful for all-optical and electromagnetic sensing, however they may have some importance for the characterization of nanoplasmonic devices in general.**

Keywords **— Electromagnetic Propagation, Negative Permittivity, Ultralow Refractive Index, Wire Mesh Media, Nanotechnologies, Nanoplasmonics.**

I. Introduction

Electromagnetic metamaterials play an increasingly important role in extending the range of applicability of various optical and microwave devices. This is a consequence of the possibility to engineer artificial materials with electromagnetic properties not readily encountered in nature. In the optical range, this is connected with the advent of micro- and nanostructuring technologies. Probably the most well known metamaterials are those with negative refractive index (NRM) [1-3]. Others include hole arrays with extraordinary transmission [4], materials with near-zero refractive index [5-6], etc.

The possibility to fabricate designer materials with tailored electromagnetic properties was recognized relatively early. One may claim that one of the roots of practical electromagnetic metamaterials can be traced to the 1950-ties, when artificial dielectrics [7-8] were introduced for the needs of radar technology.

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One of the important directions for the investigation of designer materials is the fabrication and application of tunable structures. Their wide area of applicability covers various optical modulation systems for communications, sensing devices, control systems, etc. and includes both passive and active components. Among these, plasmon-based sensors play a special role with their applicability in environmental protection, forensic applications, defense against terrorism, etc. because of their extremely high sensitivity. The most widespread are surface plasmon resonance devices which are applicable in adsorption-based sensing [9]. Various chemical, biochemical and biological sensors, able to sense adlayer thickness changes below 0.03 atomic radii [10] are based on this mechanism. Recently this platform was extended by proposing the devices based on electromagnetic metamaterials [11, 12] and generally nanoplasmonic structures [12]. In this way the novel functionalities of metamaterials are utilized to further improve possibilities for tuning of their electromagnetic properties (for reviews of NRM see [3, 13]). Thus the investigation of the adsorption on continuous and nanostructured plasmonic surfaces has a significant practical importance.

Another reason for such investigation is that every plasmonic device must exist in some kind of a real environment, and is usually surrounded by gas, sometimes liquid. The adsorption of that fluid will modify its properties, and the amount and kind of the modification will depend on the fluid composition and temperature.

In addition to that, the competing adsorption and desorption processes will cause a noise component to limit the operation of such a device. Although the adlayer thickness may be down to the order of a nanometer or less, its influence to the electromagnetic performance will be far from non-negligible, because the evanescent propagation of waves which is the very basis of the operation of such devices will be nevertheless greatly affected [12].

In this paper we analyze tunable structures based on wire-mesh media [2,14,15]. We model the influence of thin dielectric layers adsorbed on the wire surface. We utilize a first-principles approach to determine the scattering parameters of the structures under investigation. We analyze the case when the mesh medium is fully immersed into analyte fluid and the situation when there is a nanometric film on the wire surface, with a thickness starting from 0.3 nm (an atomic or molecular monolayer).

II. Theory

A wire mesh medium [2,14,15] consists of a large number of thin and long (diameter 2*r* much smaller than the wire length) parallel metal wires embedded in a dielectric medium (vacuum, gas or liquid). A schematic presentation of such a medium is shown in Fig. 1. Fig. 1a shows a top view to the set of wires, while arrows indicate the direction of the incident electromagnetic wave. The structure operates in the subwavelength mode, meaning that the operating wavelength is at least several times larger than the unit cell length *a*.

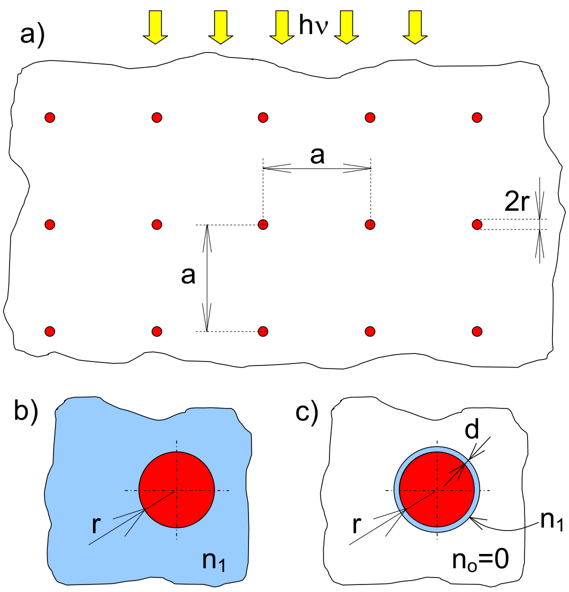

Fig. 1. a) Basic geometry of the wire mesh structure under consideration for normal incidence of light: wire radius *r*, unit cell step *a*; b) wire mesh completely immersed in medium with a refractive index n_1; c) wire mesh with a thin adsorbed surface layer (thickness *d*, refractive index n_1).

Wire mesh medium can be fabricated for various ranges of the electromagnetic spectrum from microwave to visible. The majority of such media until now was produced for the microwave, in order to artificially obtain negative dielectric permittivity [2]. However, our intention here is to consider the applicability in the visible. For that range, the unit cell length should be 100 nm or less, while a convenient wire diameter should be 10-20 nm. Wire mesh media with such dimensions are readily obtained by various nanowire fabrication techniques in metals [16], for instance by chemical deposition, electrodeposition, physical and filling of carbon nanotubes. Also highly conductive oriented carbon nanotubes [17] are available for the same purpose.

The relative dielectric permittivity of wire mesh medium has a plasma-type frequency dependence

$$\varepsilon_{\mathrm{r\ eff}} = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}. \qquad (1)$$

where ω_p denotes the plasma frequency, while γ is the damping frequency, describing losses. Thus spectral $\varepsilon_{\mathrm{eff}}$ has the well-known Drude shape, starting from negative values near and above the plasma frequency, reaching a zero-value and continuing to be positive at still larger wavelengths. The idea here is to use the wire mesh medium at the critical frequency near its zero-permittivity point.

Since magnetic permeability is approximately 1 for non-ferromagnetic materials, the refractive index will also be close to zero, assuming a form

$$n_{\mathrm{eff}} = 1 - \delta + i\beta \qquad (2)$$

where $\delta \approx 1$ while β describes absorptive losses which are unavoidable in a metal-containing matrix. This kind of artificial structure has been denoted as ULIM, Ultra-Low refractive Index Material [5, 6]. A detailed analysis of wire mesh media can be found in [18].

Fig. 1b shows a single wire completely immersed in a fluid with a refractive index n_1, while 1c shows the wire with an adsorbed layer n_1 with a thickness *d*, $d<<r$. In the case 1c the structure (wire + adlayer) is surrounded by vacuum or air, n_0=0. It is worth mentioning that the situation 1c may be actually reduced to the 1b by applying the effective medium approach. In both cases the effective refractive index is modified by the presence of the adsorbate. This is similar to the operation of surface plasmon devices, however with an important difference that the adsorbing material is nanostructured. Thus the effective adsorbing surface is largely increased (the case of "catalyst plus" [12]) and at the same time spread throughout the volume of the medium.

In the presence of adsorbate the effective index of the wire mesh will be modified as

$$n'_{\mathrm{eff}} = n_{\mathrm{eff}} + \Delta n \qquad (3)$$

where Δn is the change introduced by the adsorbate. Since $\mathrm{Re}(n_{\mathrm{eff}}) \approx 0$, the contrast between the initial and the modified value of the refractive index will be large and thus measurable in spectral reflection near the zero-ε point.

III. Results

We performed our calculation for a 2D square lattice of metal wires utilizing the finite element approach. We applied periodic boundary conditions to simulate an infinite structure. The dimensions of the wire mesh were 10 nm diameter, 120 nm period (unit cell constant) in both transversal and longitudinal direction, while the wire length was assumed to be infinite.

A perfect electrical conductor (PEC) was assumed for the wire material, its electrical conductivity in the frequency range under consideration being $\sigma=10^{30}\ \mathrm{S\cdot m^{-1}}$ while the initial surrounding medium was air, ε_r=1. We performed our calculation for an incident wave direction perpendicular to the wires, its electric field vector parallel with the wires. We calculated the reflection coefficient (scattering parameter S_{11}) for our wire mesh medium.

First we analyzed the case of full immersion of the wire medium into dielectric analyte, as shown in Fig. 1.

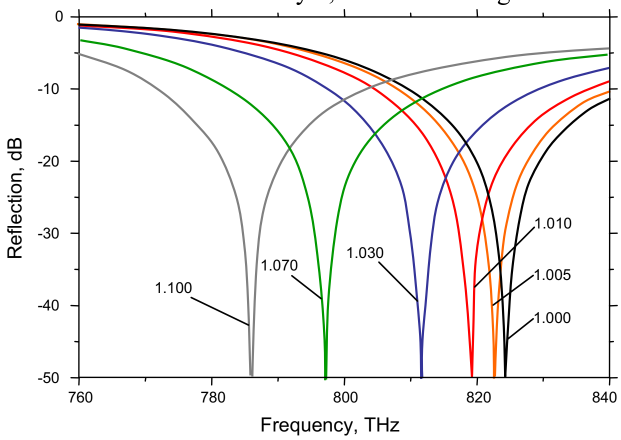

Fig. 2. The case of full immersion of wire mesh: spectral reflection for various permittivities of the immersing fluid (ε values denoted by the corresponding curves)

Fig. 2 shows spectral reflection for various permittivities of immersing fluid.

The reflection minimum is located in the visible range and the increase of the relative permittivity shifts the dip toward larger wavelengths. It can be seen that a significant shift of the spectral curve is observed even for relatively small relative permittivity changes.

Fig. 3 shows the results for an especially interesting case of thin dielectric adlayer formed on the wires surface. Realistic situations are assumed: the case without adlayer, the adlayer thickness 0.3 nm (corresponding to a monolayer of atoms or molecules) and 0.5 nm to 5 nm (corresponding to multilayer adsorption). All of these situations are of interest when considering electromagnetic properties of real plasmon devices. We assumed a value of adlayer relative permittivity of 1.5.

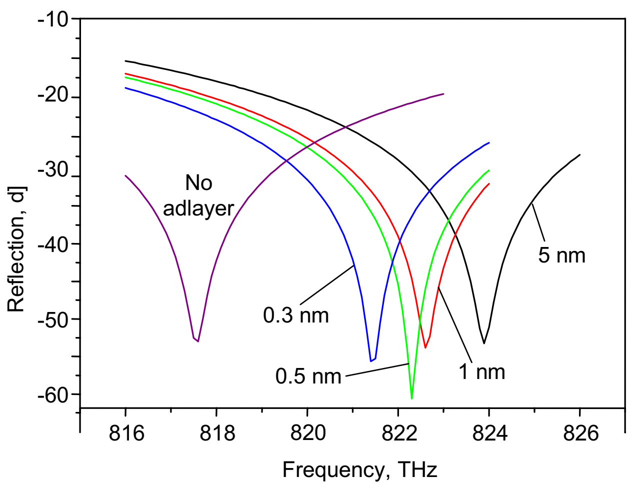

Fig. 3. The case of thin adlayer on wire mesh: spectral reflection for various values of adlayer thickness ($\varepsilon_r = 1.5$)

Again a significant frequency shift of the reflection dip is observed. Adlayer thickness increase shifts the dip towards higher frequencies.

Fig. 4 shows the dependence of the reflection minimum frequency on the adsorbed layer thickness. The obtained curve is slightly nonlinear.

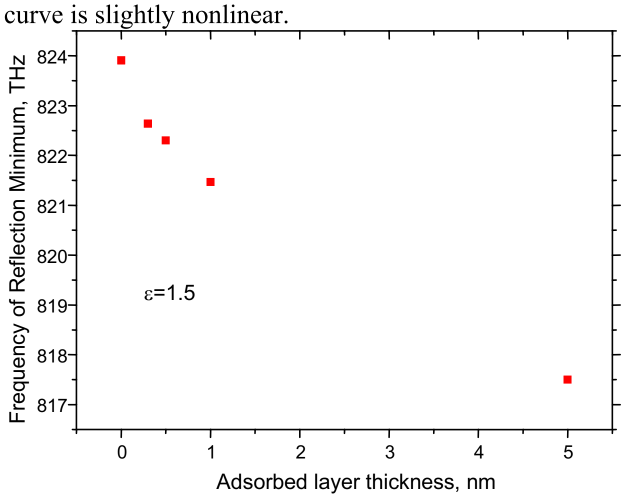

Fig. 4. Reflection dip frequency versus adsorbed layer thickness for an adlayer relative permittivity value of 1.5

In Fig. 5 we investigated the influence of finite electrical conductivity of wire material and considered the application of real metals at room temperature.

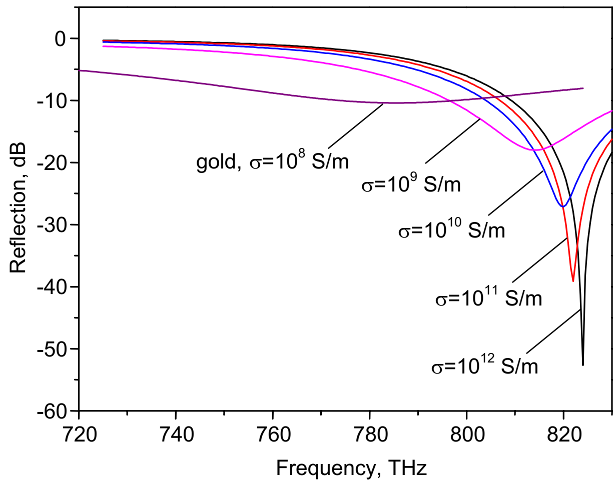

Fig. 5. Influence of finite conductivity on the shape of spectral reflectance dip

As expected, the reflection minimum is smoothened because of the finite conductivity. However, it is interesting to observe that even relatively low conductivities of about 10^{10} $S \cdot m^{-1}$ preserve the reflection peak. It is also visible that conductivity decrease slightly shifts the peak to lower frequencies.

It should be mentioned that even larger conductivities than those presented in Fig. 5 are available with certain materials and/or at low temperatures (for instance, high conductance carbon nanotubes and nanotubes generally, also superconductors with high critical temperature)

IV. Conclusion

We studied the possibilities to tune the properties of wire mesh medium by either immersion in dielectric gas or liquid or the adsorption of a thin dielectric film on the wire surface. We utilized finite element modeling to determine the influence of various parameters on spectral reflection of the wire mesh medium. Relatively large shifts of frequency tip were observed even for effective relative permittivity changes of the order of 0.5% and adlayer thickness values corresponding to an atomic monolayer. As expected, losses impair the overall sensitivity of the structure to relative permittivity or thickness changes, however the existing materials are sufficient to ensure satisfactory performance. We believe the structure can be utilized in high-sensitivity chemical, biochemical and biological electromagnetic sensing (e.g. for environmental protection, forensic applications, defense against terrorism, etc.)

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