Copper-Nickel heterometallic multilayer composites for plasmonic applications

Ivana Mladenović, Zoran Jakšić, *Senior Member, IEEE*, Marko Obradov, Slobodan Vuković, Goran Isić, Jelena Lamovec

***Abstract*— Plasmonics and optical metamaterials offer possibilities for numerous applications in different fields, from transformation optics and chemical sensing to merging the beneficial properties of electronic and optical circuits. Crucial for their function are interfaces between materials of which one has to exhibit negative value of relative dielectric permittivity due to the existence of free electron plasma. However, the choice of convenient materials is rather limited and their performance is severely impaired by strong absorption losses. This is the reason why alternative plasmonic media are currently of an increasing interest. In this contribution we consider one such medium, the heterometallic multilayer consisting of copper and nickel. Copper is an excellent plasmonic material, but needs protection against surface oxidation, a role fulfilled by nickel layers which simultaneously form interfaces supporting surface waves. We describe our proposed heterometallics and consider their electromagnetic properties and experimental fabrication. *Ab initio* numerical simulations were done using the finite element method for Cu-Ni multilayers on a copper substrate. Laminate composite structures of alternately electrodeposited nanocrystalline Ni and Cu films on cold-rolled polycrystalline copper substrates were fabricated. Highly-densified parallel interfaces can be obtained by depositing layers at a very narrow spacing. Our results show that Cu-Ni pairs are a viable alternative to conventional plasmonic media, while the electrodeposition approach offers acceptable structural and electromagnetic parameters with large area and good uniformity at a low cost.**

***Index Terms* — Plasmonics; Heterometallics; Optical Multilayers; Copper-Nickel Films; Electrodeposition**

I. Introduction

FROM the electromagnetic point of view, the existence of interfaces between materials with different relative dielectric permittivity and/or relative magnetic permeability results in a wealth of different electromagnetic modes supported by such structures. The simplest case is a contact between two semi-infinite uniform materials, one of them with negative relative permittivity (i.e. having free electrons as charge carriers) and the other with positive permittivity. If electron plasma frequency coincides with or is sufficiently near to the electromagnetic wave frequency, a new mode appears defined by the resonant oscillations of electrons. It is p-polarized and bound to the interface between the two materials, exponentially decaying in both perpendicular directions – the surface plasmon polariton (SPP). More complex composites introduce a wealth of new modes. The branch of electromagnetic optics making use of the resonant properties of free electrons is called plasmonics [1, 2]. The existence of the SPPs and similar surface phenomena ensures extreme localizations of fields in subwavelength volumes [3,4].

More generally, the possibility to design electromagnetic modes at will opens the gate to arbitrary tailoring and transforming the optical space. This is called transformation optics [5], and plasmonics ensures its use in the optical frequency range. Various applications include chemical and biological sensors [6], circuits that merge compactness of electrical circuitry with high frequencies of all-optical devices [7], superabsorbers and superlenses, super-resolution lithography [8], to name just a few.

One of the problems with the use of materials with free electron plasma are their high absorption losses caused by intra- and inter-band electronic transitions. Another is related with the available operating frequency ranges. These are some of the reasons why alternative plasmonic materials are constantly being sought after. The most common choice for plasmonics are gold and silver, both offering excellent conductivity and the possibility to be processed using the standard microsystem techniques. Other proposed materials include transparent conductive oxides, heavily doped semiconductors, intermetallics, etc. [9, 10]

Copper is one of the materials with properties very convenient for plasmonics. A problem is that exposed to atmosphere it quickly oxidizes, which can impair the performance of nanometer-thick structures used in plasmonics or even completely remove any desirable effects. In spite of this, copper is sometimes used in plasmonics, combined with some means to protect its surface.

Here we report on the design and fabrication of alternating copper-nickel multilayers, where nickel serves a dual purpose of ensuring multiple plasmonic interfaces with copper and providing protection against environmental influences.

Ivana Mladenović is with Centre of Microel. Technologies, Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia (e-mail: ivana@nanosys.ihtm.bg.ac.rs).

Zoran Jakšić is with Centre of Microelectronic Technologies, Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia (e-mail: jaksa@nanosys.ihtm.bg.ac.rs).

Marko Obradov is with Centre of Microel. Technologies, Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia (e-mail: marko.obradov@nanosys.ihtm.bg.ac.rs).

Slobodan Vuković is with Centre of Microel. Technologies, Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia (e-mail: svukovic@nanosys.ihtm.bg.ac.rs).

Goran Isić is with Center for Solid State Physics and New Materials, Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia (e-mail: isicg@ipb.ac.rs).

Jelena Lamovec is with Centre of Microel. Technologies, Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia (e-mail: jejal@nanosys.ihtm.bg.ac.rs).

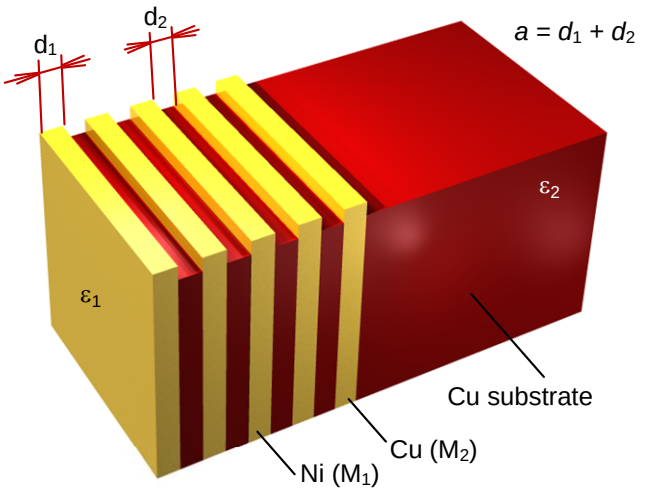

Fig. 1. Geometry of our heterometallic multilayer. Surface relief is visible at the top of the structure.

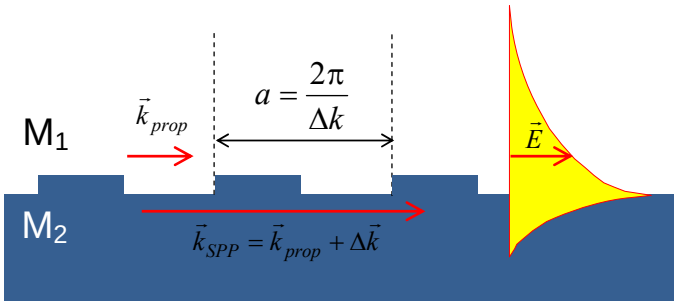

Fig. 2. Coupling between the SPP and the propagating beam on a diffractive grating (in this case the surface relief on the Cu-Ni multilayer). M_1 and M_2 denote nickel and copper (metal 1 and metal 2), respectively. Yellow area shows the intensity of the electric field of the SPP versus distance from the interface.

II. Theory

We investigate a multilayer structure with alternating strata of two different materials (metals M_1 and M_2,) each of them uniform and homogenous, each described by its complex relative dielectric permittivity ($\varepsilon_1(\omega) = \varepsilon'_1 + \varepsilon''_1$ and $\varepsilon_2(\omega) = \varepsilon'_1 + \varepsilon''_2$) and by its thickness ($d_1$ and d_2). We assume that the relative magnetic permeabilities of the both constituents $\mu_1(\omega)$ and $\mu_2(\omega)$ are equal to 1 since we consider the optical frequency range.

The geometry of the heterometallic multilayer is shown in Fig. 1. The multilayer is deposited onto a copper substrate. We assume that the relative dielectric permittivity of each metal is well described by the lossy extended Drude model [1]

$$\varepsilon_j(\omega) = \varepsilon_{\infty j} - \frac{\omega_{pj}^2}{\omega^2 + i\gamma_j\omega}, \quad j = 1,2 \qquad (1)$$

where ω_p is the plasma frequency of the electron plasma, ε_∞ is the asymptotic dielectric permittivity and $\gamma=1/\tau$ is the characteristic frequency related to the damping of electron oscillations due to collisions, where τ is the relaxation time of the electron gas.

Since both M_1 and M_2 are plasmonic materials, the multilayer structure shown in Fig. 1 represents the general case of finite one-dimensional, two-material plasmonic crystal [11, 12]. We denote the electromagnetic wave propagation perpendicular to the multilayer surface by the Bloch wave vector $\vec{q}$. The propagation of a surface wave along an interface between the two different materials M_1 and M_2 is described by the plasmonic wave vector $\vec{k}$. We denote the number of the layer pairs by N, and the total thickness of a single layer pair by $a = d_1 + d_2$.

We proceed by writing the spectral dispersion relation connecting the frequency and the wave vector within the given structure. The usual way to obtain the dispersion of a finite plasmonic crystal is to utilize the transfer matrix method [13–15]. The dispersion relation is obtained as

$$\frac{1}{2}(T_{11} - T_{22}) = -\mathrm{cotg}(Nqa)\sin(qa), \qquad (2)$$

$$\frac{1}{2}(T_{11} + T_{22}) = \cos(qa), \qquad (3)$$

where T_{11} and T_{22} are the diagonal transfer matrix elements. Written for the electromagnetic waves outside the light cone and for S-polarized waves these elements are

$$T_{11} = \exp(i\kappa_m d_{m1})\left[\cosh(\kappa_{m2}a - \kappa_{m2}d_{m1}) - \frac{1}{2}\left(\frac{\kappa_{m2}}{\kappa_{m1}} - \frac{\kappa_{m1}}{\kappa_{m2}}\right)\sinh(\kappa_{m2}a - \kappa_{m2}d_{m1})\right], \qquad (4)$$

$$T_{22} = \exp(-i\kappa_m d_{m1})\left[\cosh(\kappa_{m2}a - \kappa_{m2}d_{m1}) + \frac{1}{2}\left(\frac{\kappa_{m2}}{\kappa_{m1}} - \frac{\kappa_{m1}}{\kappa_{m2}}\right)\sinh(\kappa_{m2}a - \kappa_{m2}d_{m1})\right]. \qquad (5)$$

whereas for P-polarized waves outside the light cone

$$T_{11} = \exp(i\kappa_m d_{m1})\left[\cosh(\kappa_{m2}a - \kappa_{m2}d_{m1}) - \frac{1}{2}\left(\frac{\kappa_{m2}\varepsilon_{m1}}{\kappa_{m1}\varepsilon_{m2}} - \frac{\kappa_{m1}\varepsilon_{m2}}{\kappa_{m2}\varepsilon_{m1}}\right)\sinh(\kappa_{m2}a - \kappa_{m2}d_{m1})\right], \qquad (6)$$

$$T_{22} = \exp(-i\kappa_m d_{m1})\left[\cosh(\kappa_{m2}a - \kappa_{m2}d_{m1}) + \frac{1}{2}\left(\frac{\kappa_{m2}\varepsilon_{m1}}{\kappa_{m1}\varepsilon_{m2}} - \frac{\kappa_{m1}\varepsilon_{m2}}{\kappa_{m2}\varepsilon_{m1}}\right)\sinh(\kappa_{m2}a - \kappa_{m2}d_{m1})\right]. \qquad (7)$$

These equations are also applicable for the waves inside the light cone, but in this case hyperbolic functions in T_{11}, T_{22} should be replaced with the corresponding regular trigonometric functions.

The next point of interest is the surface relief visible on the top of the sample in Fig. 1. An idealized view of the obtained profile is shown in Fig. 2. The existence of the relief is convenient to ensure coupling between SPPs and a propagating interrogation beam without a need to utilize inconvenient external beam couplers needed for the conventional plasmonic structures.

It is well known that to couple propagating and surface waves one needs to impart additional momentum Δk to the propagating wave [1]. One of the methods of coupling is the use of a diffractive grating [2]. In our case the heterometallic multilayer itself represents such a grating. Technologically the necessary relied can be produced in a simple way by selectively etching the copper part of the heterometallic layer.

The well-known relation between the diffractive grating constant $a = d_1 + d_2$ and the wave vector of the diffracted mode is

$$\Delta k = \pm m \frac{2\pi}{a} , \tag{8}$$

where m is an integer. Thus matching is obtained if

$$\vec{\kappa} = \vec{q} + \Delta\vec{k} , \tag{9}$$

where the propagating mode is

$$q = \frac{\omega}{c} \sin\theta . \tag{10}$$

here ω is the angular frequency, c is the speed of light in the medium above the plasmonic surface and θ is the incident angle of the propagating mode.

III. Numerical

We examined the scattering of a plane wave incident on the structure in Fig. 1 using the finite element method. To this purpose we utilized the RF module of Comsol Multiphysics software package. The modeled structure consisted of four nickel layers and three copper layers deposited on a copper substrate. For the purpose of our simulation the substrate was assumed sufficiently thick to be considered infinite. The structure was surrounded by air.

Our simulations calculated the scattered waves as a perturbation caused when our structure is introduced into a background electromagnetic field described by a propagating plane wave. Since the background medium is homogenous (air) it is possible to set the background field by simply using the analytic expression for the plane wave. The entire domain was encased in a perfectly matched layer (PML) acting as a perfect absorber and preventing unwanted internal reflections by collecting scattered radiation. The total field representing the optical response of the structure was calculated as a superposition of the scattered and the background fields.

Figs. 3 and 4 show examples of the incident wave coupling with the plasmonic modes of our structure for oblique incidence. Fig. 3 shows a d_1=100nm, d_2=300nm structure for 750 nm incident radiation. A selectivity of light localization in the copper channels is observed when changing the angle of incidence from 30º to 60º. Coupling of the incident wave with the surface modes on the copper substrate is shown in Fig. 4 for a 60º incident angle. The frequency and the strength of the coupling are both dependent on the grating period. We observed a blue shift of the resonant wavelength from 850 nm to 670 nm when the thickness of the layers was changed from d_1=100 nm, d_2=300 nm to d_1=200 nm, d_2=500 nm.

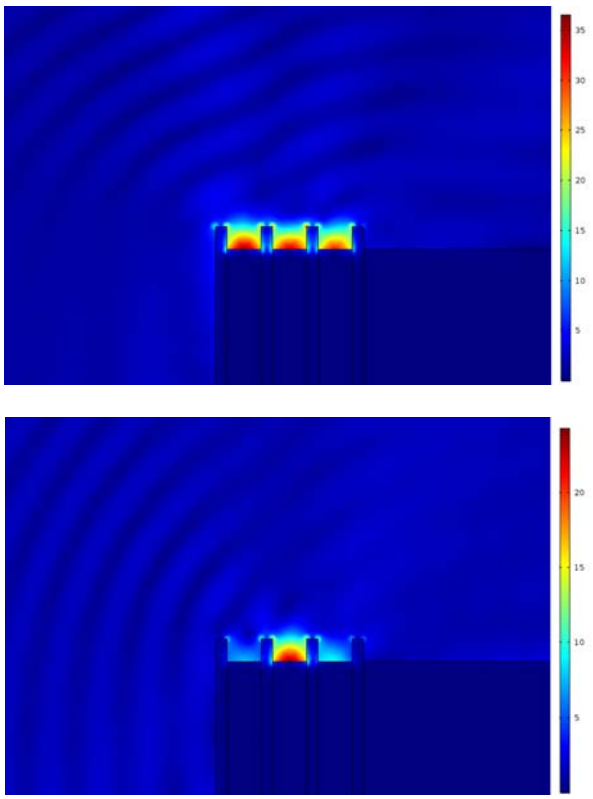

Fig. 3. Total electric field intensity for d_1=100 nm, d_2=300 nm structure at 750 nm for: a) 30º incident angle and b) 60º incident angle.

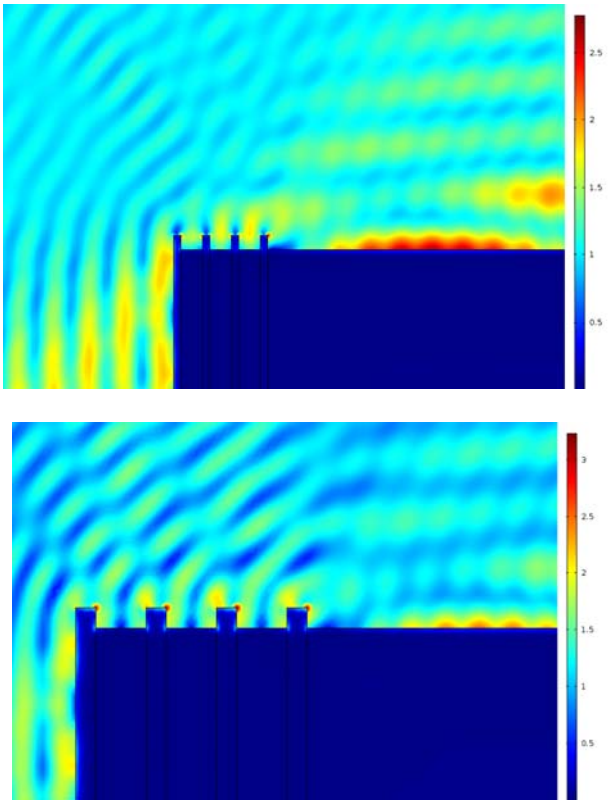

Fig. 4. Total electric field intensity for: a) d_1=100 nm, d_2=300 nm structure at 670 nm and 60º incident angle; b) d_1=200 nm, d_2=500 nm structure at 850 nm and 60º incident angle.

IV. EXPERIMENTAL

For our experiments we used electrochemical deposition since it is fully compatible with MEMS technologies and offers a high controllability of the deposition rate, thickness and residual stress in Ni and Cu deposits [16, 17].

The substrate for electrodeposition of Ni and Cu thin films was a 125 μm thick copper foil. Prior to deposition, the substrate was degreased and chemically polished in acid mixture.

Electrochemical deposition was carried out using direct current galvanostatic mode with the current density values maintained at 10 mA/cm^2 and 50 mA/cm^2. The deposition time was determined in dependence on the plating surface and the projected thickness of deposits.

Ni and Cu films were electrodeposited separately from two different electrolytes. This technique is known as the Dual Bath Technique (DBT).

Copper films were electrodeposited from a sulfate bath consisting of 240 g·l^{-1} $CuSO_4 \times 5H_2O$ (1M $CuSO_4$), 40.8 ml H_2SO_4 (0.77 M H_2SO_4) and deionized water. The process temperature and pH were maintained at 25ºC and 0.4, respectively. Nickel films were electrodeposited from a sulfamate bath consisting of 300 g·l^{-1} $Ni(NH_2SO_3)_2 \cdot 4\,H_2O$, 30 g·l^{-1} $NiCl_2 \cdot 6H_2O$, 30 g·l^{-1} H_3BO_3, 1 g·l^{-1} saccharine with maintained temperature and pH values at 50ºC and 4.2, respectively.

The microstructure of the laminate composite structures was investigated by metallographic microscopy (Carl Zeiss microscope "Epival Interphako") . The topographic details of the cross-section of the multilayer composite were investigated by Scanning Electron Microscope (SEM, JEOL JSM-T20).

The process of revealing the geometry of the multilayer structure started with a perpendicular cut of the deposited films. The samples were embedded in self-curing methyl methacrylate-polymer (Palavit G, Heraeus, Germany) and mechanically polished with different SiC papers and alumina powder with different grain size (1 μm and 0.3 μm). Rinsing solution of Na_2CO_3 was used to avoid the agglomeration of alumina powder. Finally the structures were dried in nitrogen flow.

The revealed microstructure of the Ni and Cu layers with different strata thickness, before sacrificial etching of copper layer in thiourea solution, is shown in Fig. 5 (total film thickness 75 μm), and in Fig. 6 (total film thickness 25 μm). The acid solution of 1 M thiourea at 40°C (pH = 1, achieved by adding HCl) was used for selective etching of copper layers and the substrate, while the nickel layers remained chemically stable.

In Fig. 7, the result of the etching process of the copper layers in acid thiourea solution is presented. The released nickel layers are clearly visible.

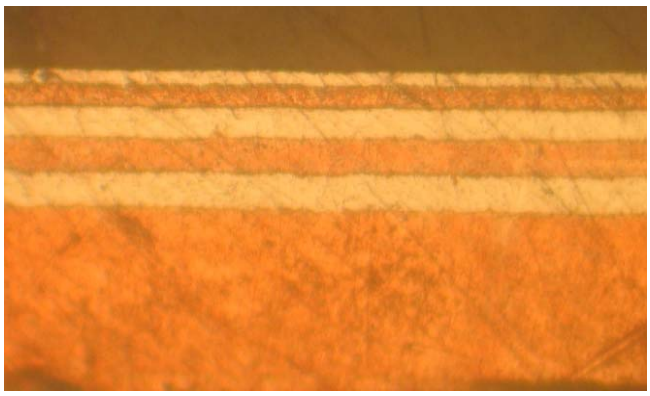

Fig. 5. Optical image of the cross-section of an electrodeposited Ni-Cu-Ni multilayer, thickness 20 μm/20 μm/20/10/5 μm, before a selective etching copper film. The current density for both film was 50 mA/cm^2

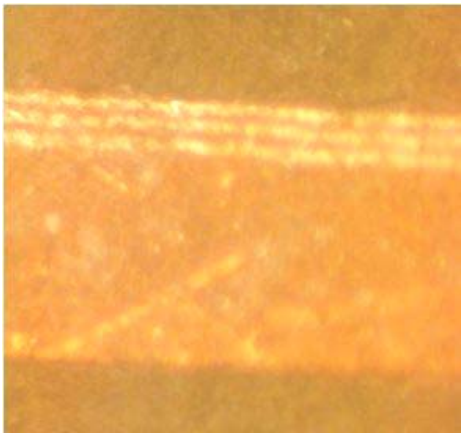

Fig. 6. Optical image of the cross-section of an electrodeposited Ni-Cu-Ni multilayer, thickness of the single film is 5 μm, number of layer is 5.

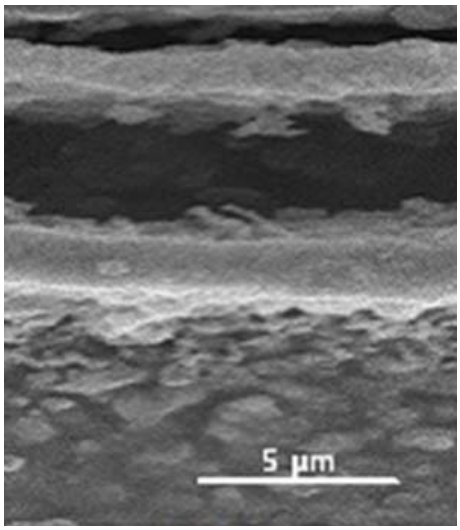

Fig. 7. SEM image of the cross-section of an electrodeposited Ni-Cu-Ni multilayer, thickness 2 μm/5 μm/2 μm.

V. Conclusion

We analyzed the applicability of Cu-Ni laminar composites as an alternative plasmonic material. It is shown that beneficial properties of 2D copper layers can be used while suppressing the undesired ones by the use of nickel. The obtained structures serve a dual purpose as a plasmonic platform and simultaneously a diffractive coupler between propagating and surface modes. Among the advantages of the utilized approach are its low cost and its high controllability over large areas, the possibility to deposit layer on non-flat structures, as well as its compatibility with the standard MEMS procedures. Our further work will consider the use of alternative substrates, as well as different other heterometallic and, more generally, heteroplasmonic platforms.

Acknowledgment

This work was supported by the Serbian Ministry of Education, Science and Technological Development under Projects No. TR32008, OI171005 and III45016, by Qatar National Research Fund under project NPRP 08-128-1-001 and by COST action MP1402 HERALD.

References

[1] S. A. Maier, *Plasmonics: Fundamentals and Applications*, Springer Science+Business Media, New York, NY, 2007.

[2] H. Raether, *Surface plasmons on smooth and rough surfaces and on gratings*, Springer Verlag, Berlin-Heidelberg, Germany, 1986.

[3] W. L. Barnes, A. Dereux, and T. W. Ebbesen, "Surface plasmon subwavelength optics," *Nature,* vol. 424, no. 6950, pp. 824-830, 2003.

[4] J. A. Schuller, E. S. Barnard, W. Cai, Y. C. Jun, J. S. White, and M. L. Brongersma, "Plasmonics for extreme light concentration and manipulation," *Nature Mater*., vol. 9, no. 3, pp. 193-204, 2010.

[5] J. B. Pendry, D. Schurig, D. R. Smith, Controlling Electromagnetic Fields, *Science,* 312, (2006), 1780-1782.

[6] I. Abdulhalim, M. Zourob, and A. Lakhtakia, "Surface plasmon resonance for biosensing: A mini-review," *Electromagnetics,* vol. 28, no. 3, pp. 214-242, 2008.

[7] E. Ozbay, "Plasmonics: Merging Photonics and Electronics at Nanoscale Dimensions," *Science,* vol. 311, no. 5758, pp. 189-193, 2006.

[8] N. Fang, H. Lee, C. Sun, and X. Zhang, "Sub-diffraction-limited optical imaging with a silver superlens," *Science,* vol. 308, no. 5721, pp. 534-537, 2005.

[9] A. Boltasseva, H. A. Atwater, Low-Loss Plasmonic Metamaterials, *Science,* 331, (2011), 290-291.

[10] P. R. West, S. Ishii, G. V. Naik, N. K. Emani, V. Shalaev, A. Boltasseva, Searching for better plasmonic materials, *Laser & Photon. Rev*, (2010), 1-13.

[11] S. M. Vuković, Z. Jakšić, I. V. Shadrivov, Y. S. Kivshar, Plasmonic crystal waveguides *Appl. Phys. A,* 103, (2011), 615-617.

[12] S. M. Vuković, Z. Jakšić, J. Matovic, Plasmon modes on laminated nanomembrane-based waveguides, *J. Nanophotonics,* 4, (2010), 041770.

[13] M. Born, E. Wolf, *Principles of Optics*, 7th ed., Cambridge University Press, Cambridge 1999.

[14] P. Yeh, A. Yariv, C.-S. Hong, Electromagnetic propagation in periodic stratified media. I. General theory, *J. Opt. Soc. Am.,* 67, (1977), 423-438.

[15] P. Yeh, *Optical Waves in Layered Media*, Wiley VCH, Weinheim 1988.

[16] J. Lamovec, V. Jović, D. Randjelović, R. Aleksić, V. Radojević, "Analysis of the composite and film hardness of electrodeposited nickel coatings on different substrates", *Thin Solid Films*, 516 (23), pp. 8646-8654, (2008).

[17] J. Lamovec, V. Jović, M. Vorkapić, B. Popović, V. Radojević, R. Aleksić, "Microhardness analysis of thin metallic multilayer composite films on copper substrates", *Journal of Mining and Metallurgy, Section B: Metallurgy*, 47 (1), pp. 53-61, 2011.