VUKOMAN JOKANOVIĆ[1,2], BOŽANA ČOLOVIĆ[2], BOJAN JOKANOVIĆ[3], STEVAN STOJADINOVIĆ[4] ANKA PETKOSKA TRAJKOVSKA[5], ILIJA NASOV[6]*

[1]ALBOS d.o.o., Belgrade, Serbia, [2]University of Belgrade, Institute of Nuclear Sciences „Vinča“, Belgrade, Serbia, [3]GL group, Metingen, Germany, [4]University of Belgrade, Faculty of Physics, Belgrade, Serbia, [5]University St. Kliment Ohridski, Faculty of Technology and Technical Sciences, Veles, R. Macedonia, [6]Plasma doo, Skopje, R. Macedonia

Scientific paper
ISSN 0351-9465, E-ISSN 2466-2585
UDC: 620.181.5:669.295.7
doi:10.5937/ZasMat1602225J

Zastita Materijala 57 (2)
225 - 231 (2016)

Plasmonic metamaterials based on titanium oxides

ABSTRACT

The basic information about any kind of metamaterials is given in this paper. Special attention is dedicated to materials on the base of titanium oxides, which have not been studied as metamaterials yet. Due to different titanium oxidative states in thin films of titanium oxides deposited by dc magnetron sputtering, which influence various conductive properties from the ones typical for dielectrics, over the ones typical for semiconductors, to the ones typical for metalloids, these materials show typical metamaterials properties. This is noticed for the first time in our investigations, which are partially presented in this paper. Huge number of band gaps influences extreme change of optical properties, particularly refractive index which changes from very high to near zero values. Reasons for that behaviour are explained over corresponding splitting of molecular orbitals.

Key words: *metamaterials, plasmonics, titanium oxidative states, band gaps, ultra high and zero refractive indices.*

1. INTRODUCTION

Strong resonances appeared at optical frequencies for metal nanoparticles are induced by the resonant oscillation of free electrons on the surface of the particles and belong to the so called localized surface plasmon resonances (LSPRs) which are optical phenomena that preferentially occur in metallic nanoparticles in which collective charge motions confined at metal-dielectric interfaces can be driven into a resonant state by an incident light at a particular wavelength and polarization state [1, 2]. Typically, a plasmonic resonance assumes introduction of sufficient free carriers into the nanocrystals or sub-nanocrystals formed in thin layers of nanometric films on the base of titanium oxides, either as atomic vacancies or dopant of aliovalent cations [3, 4]. The LSPR frequency is dependent on the inherent frequency of plasmonic waves of the used material, influenced by material's properties such as carrier concentration and the type of carrier. Unlike in the case of metals, this frequency can be considered as an intrinsic property of the material, while in semiconductors it is dependent mostly on dopant concentration.

Optical resonances cause a decrease of dielectric permittivity ε for shorter wavelengths than one critical value λ, after which the dielectric permittivity starts to increase [2]. This occurs because the oscillating free carriers follow the incident field for wavelengths longer than the critical wavelength and increasingly fail to do so for shorter wavelengths. This results in a sharp decrease in ε for wavelengths slightly shorter than the LSPR. A large swing in the permittivity values close to the LSPR wavelength indicates that the resonance is very strong and is able to pull ε from positive (dielectric-like) to negative (metal-like) values.

Bearing in mind that plasmas can sustain ion and electron oscillations formed by dilatational wave of the electron density, it follows that surface plasmons (SPs) are collective oscillations of charges at the surface of plasmonic materials [5]. Consequently, SPs can be excited or coupled with the different quantized energies, *i.e.*, photons, electrons and phonons. It means that SPs coupling with photons can form the composite particles of surface plasmon polaritons (SPPs) [6].

*Corresponding author: Vukoman Jokanović
E-mail: vukoman@vin.bg.ac.rs
Paper received: 23. 03. 2016.
Paper accepted: 25. 04. 2016.
Paper is available on the website: www.idk.org.rs/journal

Besides, the half-filled bands in transition elements and energy of various plasmonic waves associated to various kinds of electron transitions between high occupied levels inside valence bands and low occupied levels in conduction band significantly influence the values of the corresponding energy gaps. For their lower values, for electrons in high occupied valence band close to Fermi level, characteristic for titanium oxides (Ti_xO_y) with different titanium oxidative states with highly pronounced metallic or semiconducting properties, the incident electromagnetic light waves inside of such structures can induce the resonance of plasmonic waves due to strong oscillation of free electrons in the overlapped valence and conduction band, influencing extraordinary high refractive index [7].

The gradient distribution of the vacancies through the Ti_xO_y film, deposited on the glass substrate, from the top towards the glass substrate surface induce appearance of the various semiconducting or metallic Ti_xO_y phases through the film depth [7]. On the top level, prevailing crystal phase is anatase or rutile, emerged inside of the amorphous phase. This layer is dielectric. In the first levels below this level, Ti_2O_3 and Ti_3O_5 phases are mostly present inside of amorphous matrix as dielectric phases. Finally, levels with preferential content of metallic phase are close to the substrate, emerged in amorphous dielectric phase. This is one rough picture of phase composition following the change of the vacancy concentration within the film depth. It seems that inside each layer the basic condition is fulfilled, that very small particles of metallic or semiconducting phases are distributed inside of the dielectric phases, with very small energy gaps, enabling the overlapping of conduction and valence band on the surface of the active metallic phase and dielectric phase. The distance between these crystal phases is shorter than the wavelength of the light electromagnetic waves, which is one of the conditions following Veselago rules for crosslinking of the plasmonic waves and its interference with electromagnetic light waves [8].

The concentration of the metallic and semiconducting phases which occupy the states at the bottom of conduction t_{2g} band is large enough for overlapping of the electronic wave functions of plasmonic waves, forming a zone of interacting particle. Oxygen vacancies collected around corresponding metallic or semiconducting Ti oxide phases show similar effect. The decrease of the electron energy induced by Coulomb forces and corresponding screening effect induce also lowering of the energy of the conduction band edge. All these induce additional effects of band-gap shrinkage. This shrinkage is mostly influenced by a free-carrier density (concentration of vacancies and electrons in conduction band) and average inter-particle spacing. The largest changes in refractive index are near the band gap; it is positive for energies below the band gap, as a result of the increase in absorption coefficient for fixed energies. The band filling and band gap shrinkage effects are very important for interband transitions, because the absorption of the photon of incident wave is high enough to move the electron within a conductive band. In the Drude model, the intraband free-carrier absorption, known as the plasma effect, is directly proportional to the concentration of electrons and holes and the square of the wavelength [9]. On the other hand, both the band filling and band gap shrinkage effects on refractive index are largest near the band gap, inducing both ultrahigh and near zero refractive indices, depending of the interference of the plasmonic and light electromagnetic waves.

2. METAMATERIALS AND PLASMONICS: THEIR DESIGN AND STRUCTURE

SP waves frequently appear at the interface between a medium with a negative value of relative dielectric permittivity and a medium with a positive one [5]. Thus the surface of metamaterials with negative refractive index will also support surface plasmons. SP waves can be induced by using metamaterials with appropriate metal-dielectric surface properties suitable for tuning plasmons termed as "designer" or "spoof" plasmons [10]. Namely, when certain surface perturbations (e.g. holes) are introduced into a structure which already supports surface plasmons (metal or metamaterial), the designer plasmons and the real plasmons merge to the point of being practically indistinguishable. In that case such plasmon complexes may be denoted as hybrid surface plasmons.

The phase composition, particularly contact between dielectric and semiconducting or metallic phases induce a variation of the refractive index, which is almost entirely based on the real part of the index (refractive index is fully described as the sum of the real and imaginary parts: $n = n_r + i\alpha$ where n_r, is the real part and α is the imaginary part depicting both loss and gain). In addition, it is well known that in semiconductor devices and metals, the imaginary part of the refractive index can be used to manipulate the phase of propagating light. Since propagation in all optical waveguides is dependent on scattering, the Fresnel coefficient is often the underlying parameter that determines the efficiency and direction of propagation.

Nevertheless which kind of application is requested, metamaterials with such properties can be provided by using our innovative approach in

the application of methods for nanometric thin film deposition, like cathodic arc deposition and DC and pulse magnetron sputtering [7]. Unusual combination of these methods (which will be showed in details in our further references) with well adjusted parameters of deposition, enabling perfect homogeneity of the deposited thin films through their depth (constituted mostly of amorphous phases, with prevailing presence of oxygen vacancies of order of 10 at%) make them very sensitive for various kinds of metamaterials and plasmonic applications due to specific electronic transitions inside these materials, either between energy states inside of valence band, or transitions between high occupation levels of valence band and low energy levels of conductive bands.

Thanks to phase inhomogeneities, influenced by various valence states of Ti in titanium oxides in some spots of these almost epitaxial structures, which roughness is negligible (cannot be seen on SEM even under the magnification of 200.000x), they are very sensitive to resonance phenomena leading to diverse very attractive potential application of these materials [7]. Various valence/oxidative states of titanium ion in some spots influenced by different behavior of diverse phases like TiO and Ti_2O (phases with metallic properties), Ti_2O_3, Ti_3O_5, Ti_4O_7 (phases with semiconducting properties) and anatase, rutile, or amorphous phase with Ti^{4+} oxidative state, induce unexpected high refractive indices and small extinction coefficients of these materials.

It is important to remark that all Ti compounds are in octahedral coordination but the polyhedra show variable distortion. For example, metallic TiO phase has a defective NaCl structure with equal numbers of randomly distributed vacancies on the cation and anion positions, while semiconducting phases Ti_2O_3 has corundum structure and Ti_3O_5 has monoclinic structure [11]. Ti atoms in Ti_3O_5 are octahedrally surrounded by O atoms and are located at three different crystallographic sites. The TiO_6 octahedra are linked by sharing edges and corners to form an infinite three-dimensional framework. Characteristic rows of six edge-sharing octahedra persist along the [103] direction. The row is linked to the nearest two rows by sharing three edges in the *ac* plane, while its extension along the *b* axis is realized by corner-sharing octahedra. The oxides Ti_4O_7 and Ti_5O_9 are other partially semiconducting members of the homologous series Ti_nO_{2n-1} (so-called Magnéli phases). All of them have mixed valence state oxides, whereby Ti_4O_7 has equal numbers of Ti^{4+} ($3d_0$) and Ti^{3+} ($3d_1$) positions. In the Ti_5O_9 structure the ratio of Ti^{4+} ($3d_0$): Ti^{3+} ($3d_1$) positions is 3:2. The structures of these oxide phases are similar to that of rutile because they contain rutile-like blocks, which are infinite in *x* and *y* dimensions and are *n* TiO_6 octahedra wide along the *z* dimension (*n* = 4 for Ti_4O_7 and *n* = 5 for Ti_5O_9). This infinite dimension is perpendicular to the O-deficient {121} planes of the pseudo-rutile lattice. Along the crystallographic shear planes the octahedra share faces, edges, and corners, whereas inside the rutile blocks they share only edges and corners. Both TiO_2 modifications rutile and anatase are tetragonal with slightly different space groups.

3. ELECTRON STRUCTURE AND SPLITTING OF MOLECULAR ORBITALS IN Ti_XO_Y

Seven titanium oxides cover a wide variety of electrical properties, showing the peculiarity of electronic structure of each phase. Cubic TiO shows metallic conductivity over a wide range of temperatures, Ti_2O_3 has an abrupt semiconductor-to-metal transition below its Neel temperature of 66 K, Ti_3O_5 has metallic conductivity just above 46 K, while Magnéli phases Ti_4O_7 and Ti_5O_9 show semiconductor-to-metal transitions, whereas rutile and anatase (TiO_2) are insulators. Such different electrical properties are induced by differences in the degree of occupancy, bond type and the strength of the interactions among the metal 3*d* orbitals and between the metal 3*d* and oxygen 2*p* orbitals.

The molecular-orbital energy-level diagram for Ti oxides consists of titanium 3*d*, 4*s*, and 4*p* atomic orbitals and oxygen 2*s* and 2*p* orbitals. The zero energy arbitrarily corresponds to Fermi level, which is partially filled 2*t*2*g* level in the molecular orbital (MO) diagram. The interaction between Ti 3*d* and O 2*p* orbitals raises the $2e_g$, $1t_{2g}$, $2t_{2g}$, and $3e_g$ MO levels, where the first two of them belong to bonding and the latter two to antibonding orbitals. The σ bonds are formed from the e_g orbitals, and the π bonds from t_{2g} orbitals. There is also an interaction between O 2*p* orbitals with the Ti 4*s* and 4*p* orbitals, which form $2a_{1g}$, $2t1u$, $3t_{1u}$, $3a_{1g}$, and $4t_{1u}$ MO levels. The $1a_{1g}$, $1t_{1u}$, and $1e_g$ MO levels correspond to slight interactions between ligand 2*s* and metal 3*d*, 4*s*, and 4*p* orbitals. The t_{2u} and t_{1g} levels are nonbonding oxygen 2*p* lone pairs. All of the Ti oxides have the same MO arrangement. The levels below the $2t_{2g}$ level are completely filled with electrons. The major difference in the electron structure of the main three Ti oxides (TiO, Ti_2O_3 and TiO_2) is the degree of occupancy of the $2t_{2g}$ level. TiO has two $2t_{2g}$ electrons, Ti_2O_3 has one, and TiO_2 has none. [7]

The values of band gaps are induced preferentially by differences in the local environment, for various titanium oxide phases, which induce a variable degree of distortion of the coordination octahedra among the studied Ti oxides. An

octahedral ligand field causes the five Ti degenerate *d* states in the conduction band to split into the two fold e_g($d_{z2}$and d_{x2-y2} orbitals) and the threefold t_{2g}(d_{xy}, d_{yz}, and d_{xz} orbitals) states. The d_{z2} and d_{x2-y2} orbitals are directed at the ligands, and the d_{xy}, d_{yz}, d_{xz} orbitals are directed between the O atoms.

The experimental spectra, also consist of two main peaks originating from transitions between O 1*s* and 2*p* σ* states that are hybridized with empty Ti 3*d* orbitals. The splitting into two peaks is due to t_{2g}-e_g splitting of the Ti 3*d* levels and the intensity is related to the degree of covalence between O atoms and Ti. These bands are influenced by transitions from O 2*p* states that are hybridized with Ti 4*s* and 4*p* states. The other transitions can be explained through interactions between O 2*p* orbitals and Ti 4*s*/4*p* orbitals. Additionally, in orthorhombic distortion $4t_{1u}$ level splits into 3 sublevels $4b_{1u}$, $4b_{2u}$, and $4b_{3u}$. Numerous possible splitting and energy levels induced various values of band gaps, and intrinsic and outer transitions, inducing as a consequence high and near zero refractive indices, typical for metamaterials and plasmonics.

4. OUR RECENT INVESTIGATIONS OF BAND GAPS AND METAMATERIALS PROPERTIES OF TITANIUM COMPOUNDS

The Ti_xO_y thin films were deposited on glass substrate by DC magnetron sputtering [7]. Two samples (1 and 2) were deposited for 45 minutes and sample 2 was additionally thermally treated at 400 °C. The band gap energies of these samples were analyzed using from the spectroscopic ellipsometry data, using Tauc equation, as it is shown in the Fig.1. and Table 1.

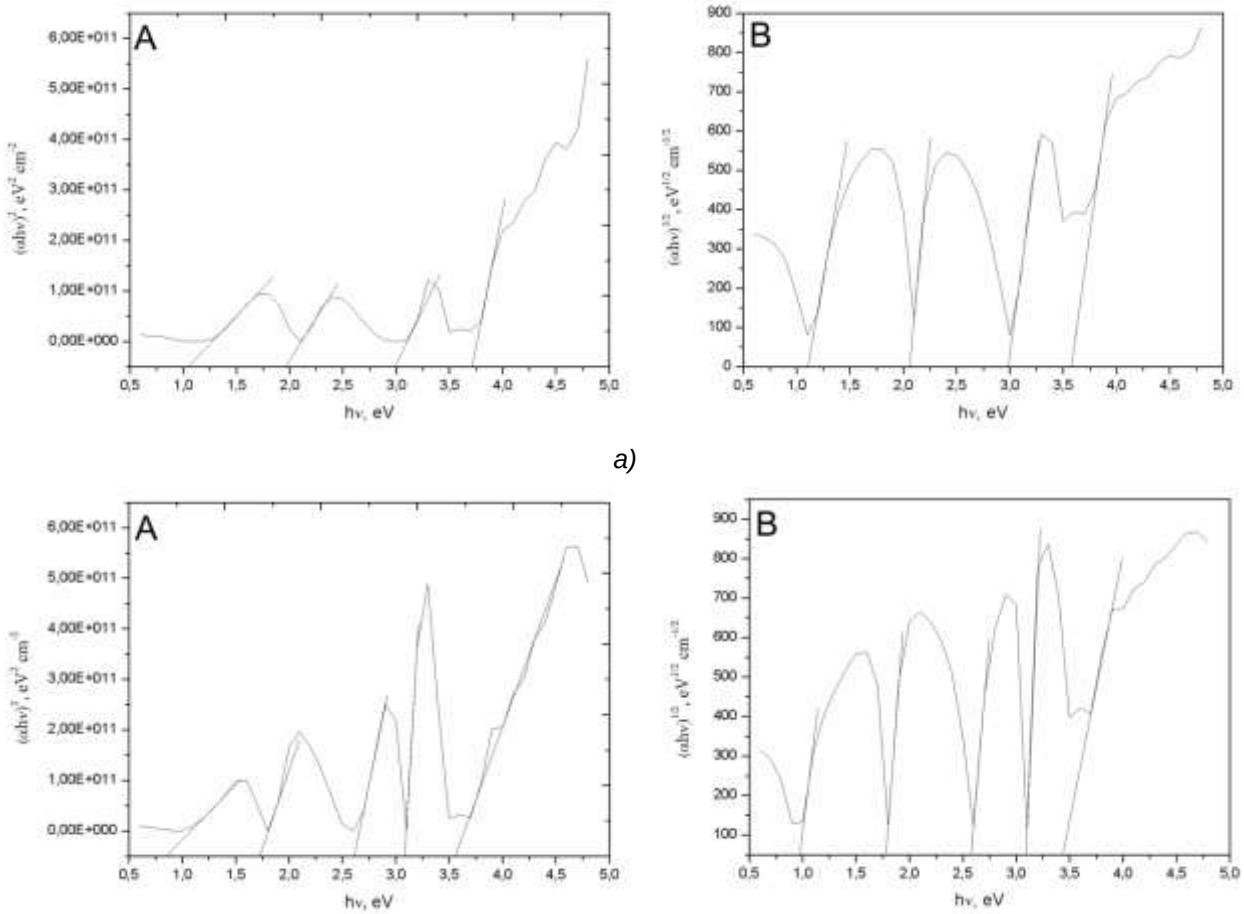

Figure 1 - Dependence $(\alpha h\nu)^{2/a}$ as a function of radiation energy hv for: a) sample 1, b) sample 2 (A- direct transition (a=2) and B- indirect transition (a=4))

Phase analysis showed that titanium is present in different oxidative states: Ti^{2+} (TiO), Ti^{3+} (Ti_2O_3), mixed Ti^{4+} and Ti^{3+} in ratio 1:2 (Ti_3O_5) and Ti^{4+} (anatase, rutile) [7]. As is it explained in section 2, Ti is in octahedral coordination in all Ti_xO_y phases, surrounded by 6 O atoms, while each O atom is surrounded by 3 Ti atoms (except TiO). The site symmetry of the Ti and O atoms these oxides differs and it is fully explained in our previous reference.

Table 1 - The band gap energy of samples and corresponding wavelength

Sample	Direct transitions		Indirect transitions	
	E_g, eV	λ range, nm	E_g, eV	λ range, nm
1	1.05	729-960	1.10	945-1050
	1.97	530-588	2.05	563-590
	3.00	386-400	3.00	382-495
	3.71	318-326	3.57	318-326
2	0.85	867-1087	0.97	1127-1228
	1.73	650-688	1.78	650-688
	2.61	427-460	2.57	457-478
	3.08	386-400	3.09	387-401
	3.56	272-336	3.43	317-336

As it is explained in ref. [7], the distortion of molecular orbitals influences the splitting of Ti d orbitals into triply degenerated t_{2g} band consisting of d_{xy}, d_{xz}, and d_{yz} orbitals and doubly degenerated e_g band consisting of $d_{x^2-y^2}$ and d_{z^2} orbitals. The e_g group forms sigma bonding (σ) and antibonding (σ*) molecular orbitals (MO): $3e_g$ (σ*) in interaction with O *2p* σ orbitals; $2e_g$ (σ) and $1e_g$ (σ) in interaction with O 2s orbitals, while the t_{2g} orbitals form pi bonding (π) and antibonding (π*) orbitals: $2t_{2g}$ (π*) and $1t_{2g}$ (π) in interaction with O *2p* π orbitals. In addition, the interaction of Ti *4s* and O 2*s* orbitals leads to formation of 2*a1g* (σ) and 1*a1g* (σ) MO while the interaction of Ti *4s* and O 2*p* σ orbitals leads to formation of 3*a1g* (σ*) MO. MO 2*t1u* (σ) and 1*t1u* (σ) are formed in the interaction of Ti *4p* and O 2*s* orbitals, while in the interaction of Ti *4p* and O 2*p* orbitals 4t1u (σ, π*) non-bonding t1g (πo) and t2u (πo) MO orbitals are formed. The antibonding orbitals are empty except the 2*t2g* (π*) on the bottom of conduction band, which are partially filled in Ti_2O_3 and Ti_3O_5 (1 electron) and TiO (2 electrons). The top of the valence band is occupied by the O 2p states with non-bonding orbitals (t_{1g} (πo) and t_{2u} (πo)) at the highest energy level. [7, 11]

A splitting and rearrangement of energy sub-levels in e_g and t_{2g} orbitals in the conduction band, occurs due to distortion of octahedral crystal fields in various Ti_xO_y. High concentration of oxygen vacancies in TiO, Ti_2O_3 and Ti_3O_5, influences an additional splitting of the t_{2g} orbitals in valence band. Therefore, it is assumed that the lowest values of band gaps belong to the transition from the highest occupied molecular orbitals (mainly O 2p orbitals, in the valence band) to the lowest unoccupied Ti 3d orbitals (in the conduction band) [12]. The low values of band gap energies suggest that these phases exhibit metal (TiO) and semiconductive (Ti_2O_3 and Ti_3O_5) character and consequently metamaterials properties. The medium band gap values probably belong to phases with Ti oxidative states between Ti^{3+} and Ti^{4+}, while the highest values correspond to oxidative state Ti^{4+}, which exhibits insulator characteristics.

Ultra-high and near-zero refractive indices of Ti_xO_y samples, revealed by spectroscopic ellipsometry, which are the evidence of their metamaterial behaviour, are the result of the electronic structure of metallic and semiconductive phases in Ti_xO_y films. This structure induces interactions between light electromagnetic waves and plasmonic waves of free electrons in the conduction band and weakly bound electrons in valence band coupled with the crystallites of Ti_xO_y phases embedded in amorphous phase. Simply, the Ti_xO_y nanoparticles can be observed as a network of positive nuclei surrounded by freely oscillating electrons, which in interaction with light waves accumulate on one side of the nanoparticle, while the other remains positive. So-formed nano-dipoles have the direction opposite to the electric field of light [13] and they radiate their own waves combining with the incoming waves. The phase between the incident and the formed waves determines the value of refractive index. If the incident wave oscillates relatively slowly, the electrons can follow the wave; they are in phase and the refractive index is very high (4.2 for sample 1 and 5.1 for sample 2). If the incident wave oscillates faster than the free electrons or electrons coupled with lattices of nanocrystallites, the electrons cannot follow it, and they get out of phase and the refractive index is close to zero (0.41 for sample 1 and 0.28 for sample 2). [14]

5. POTENTIAL APPLICATIONS OF METAMATERIALS

Metamaterials (MM) are artificially structured materials with the elements which size and spacing are much smaller than the wavelength of interest [15]. The effective MM properties are not derived from the intrinsic properties of the constituent

materials used to construct metamaterials, but from newly designed structures i.e. their size, shape, geometry, orientation.

MM can be designed in various ways to have the material properties with unprecedented degrees of freedom and to demonstrate unique properties like extremely low-frequency plasmons, artificial magnetism, negative refractive index, extremely large refractive index, and strong chirality. The broad wide range of material properties which MM posses, enables manipulation with light, leading to fast development of transformation optics.

Since the most MM are composed of metals, the plasmonic effect affects the behavior of optical MM. Some Ti_xO_y phases show metalloid properties and from theoretical stand point they can be observed as metal phases. Therefore, more comprehensive investigations of plasmonic effects in such systems are needed for further development of optical MM based on dispersive metalloid phases.

MM have many useful properties which provide their application in general sensing. Maybe the most interesting of them is the fact that their effective refractive index can be tailored to very high, near zero or negative values, which cannot be achieved by natural materials. The properties of MM can be varied to obtain the desired response, by proper choice of constitutive materials and synthesis methods. These specific properties make MM suitable for various applications such as fabrication of adaptive selective lenses, tunable mirrors, cloaking devices, beam self-collimation, strong field enhancement, optical links in lumped nanophotonic circuits, biomolecular sensors, isolators, converters, optical polarizers, in micro-strip technology etc. [7, 15]. MM structures can be further functionalized with nanoparticles, nanowires and other low-dimensional metal and semi-conductor or dielectric structures, which would enhance the MM response to the desired stimulus and decrease it or prevent for the undesired ones.

The effect of ultra high and near zero refractive index of Ti_xO_y phases was used to construct UV protective eye glasses which are particularly important for patients suffering eye melanoma.

6. CONCLUSION

The basic properties and application of metamaterials on the base of titanium oxides were studied. Their electronic properties and band gap energies induced by splitting of molecular orbitals were theoretically explained. Metamaterial properties of titanium oxide materials were for the first time observed and explained in our investigations. In this paper, an example of such system was given which due to the presence of metalloid phases shows very high and near zero refractive index. Due to our experimental results given in this paper, glasses which UV protective glasses were made, suitable for eye protection in the case of eye melanoma.

Acknowledgments

This study was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 172026)

7. REFERENCES

[1] K.A.Willets, R.P.Van Duyne (2007) Localized Surface Plasmon Resonance Spectroscopy and Sensing, Annual Review of Physical Chemistry, 58, 267-297.

[2] H.Sadeghi, A.Zolanvar, A.Ranjgar (2014) Effective Dielectric Constant of Metal Chalcogenides Ag-PbSe Nanocomposite, Armenian Journal of Physics, 7, 75-86.

[3] K.Awazu, M.Fujimaki, C.Rockstuhl, J.Tominaga, H.Murakami, Y.Ohki, N.Yoshida, T. Watanabe (2008) A Plasmonic Photocatalyst Consisting of Silver Nanoparticles Embedded in Titanium Dioxide, J. Am. Chem. Soc*., 130*, 1676–1680.

[4] G.V.Naik, J.Kim, A.Boltasseva (2011) Oxides and nitrides as alternative plasmonic materials in the optical range, Optical Materials Express, 1, 1090-1099.

[5] W.L.Barnes, A.Dereux, T.W.Ebbesen (2003) Surface plasmon subwavelength optics, Nature, 424, 824-830.

[6] A.V.Zayats, I.I.Smolyaninov, A.A.Maradudin (2005) Nano-optics of surface plasmon polaritons, Physics Reports, 408, 131–314.

[7] V.Jokanović, B.Čolović, M.Nenadović, A.Trajkovska Petkoska, M.Mitrić, B.Jokanović, I.Nasov (2016) Ultra-High and Near-Zero Refractive Indices of Magnetron Sputtered Thin-Film Metamaterials Based on Ti_xO_y, Advances in Materials Science and Engineering, Vol. 2016 , p.9, Article ID 4565493.

[8] V.G.Veselago (2011) Waves in metamaterials: Their role in modern physics, Physics-Uspekhi, 54, 1161-1165.

[9] M.S.Dresselhaus (2001) Solid State Physics. Part II: Optical Properties of Solids, MIT Solid State Physics Course, p. 8-14.

[10] N.Yu, Q.J.Wang, M.A.Kats, J.A.Fan, S.P.Khanna, L.Li, A.G.Davies, E.H.Linfield, F. Capasso (2010) Designer spoof surface plasmon structures collimate terahertz laser beams, Nature Materials, 9, 730–735

[11] E.Stoyanov, F.Langenhorst, G.Steinle-Neumann (2007) The effect of valence state and site geometry on Ti L3,2 and O K electron energy-loss spectra of Ti_xO_y phases, Am. Mineral., 92, 577-586.

[12] H.J.Zhai, L.S.Wang (2010) Probing the Electronic Structure and Band Gap Evolution of Titanium Oxide Clusters $(TiO_2)_n$ - (n =1-10) Using Photoelectron Spectroscopy, J. Am. Chem. Soc., 2007, 3022-3026.

[13] M.A.Garcia (2012) Surface plasmons in metallic nanoparticles: fundamentals and applications, J. Phys. D Appl. Phys., 45, 389501.

[14] S.A.Ramakrishna (2005) Physics of negative refractive index materials, Rep. Prog. Phys., 68, 449-521.

[15] K.Yao, Y.Liu (2014) Plasmonic Metamaterials, Nanotechnology Reviews, 3, 177–210.

IZVOD

PLAZMONIK METAMATERIJALI NA BAZI TITANOKSIDA

Osnovne informacije vezane za bilo koje vrste metamaterijale date su u ovom radu. Posebna pažnja je posvećena materijalima na bazi titanoksida, koji još uvek nisu bili predmet takvih izučavanja u svetu. Zbog različitih oksidativnih stanja titana sadržanim u tankim slojevima titanoksida deponovanih pomoću dc magnetskog rasprskavanja, koja utiču da različite faze materijala i koja pokazuju različite provodne osobine od onih tipičnih za dielektrike, preko tipičnih za poluprovodnike, sve do onih tipičnih za metaloide, ovi materijali pokazuju tipična svojstva za metamaterijale. To je primećeno po prvi put u svetu u našim istraživanjima, koja su delimično predstavljena u ovom radu. Veliki broj pragova procepa utiče na ekstremne promene optičkih svojstava, naročito indeks prelamanja, koji se menja od veoma visokih vrednosti do vrednosti bliskih nuli. Razlozi za takvo ponašanje se objašnjavaju preko odgovarajućeg cepanja molekulskih orbitala.

Ključne reči: *metamaterijali, plazmonici, titanovo oksidativno stanje, energija procepa, ultra visoki i bliski nuli indeksi prelamanja.*

Naučni rad
Rad primljen: 23. 03. 2016.
Rad prihvaćen: 25. 04. 2016.
Rad je dostupan na sajtu: www.idk.org.rs/casopis