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Control of optical properties of metal-dielectric planar plasmonic nanostructures by adjusting their architecture in the case of TiAlN/Ag system

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Abstract. The multilayer $Ag/(Ti_{34}Al_{66})N$ metal-insulator-metal (MIM) heterostructures with different thicknesses of individual layers varied from several to several hundred nanometers were fabricated by DC-magnetron sputtering on the surfaces of Si single crystal wafers. The coatings structure was determined by STEM. The phase composition and crystallography of individual layers were studied by X-ray diffraction. The reflection indexes were measured in the photons energies range from 1 to 5 eV, or from 1240 to 248 nm. The spectroscopy of plasmon losses and plasmon microscopy allowed us to measure the plasmons losses characteristic energies and their surface distribution. The energies of plasmons peaks and their locations are strongly depending on Ag layers thickness in the MIM nanocomposite. The surface plasmon with energy about 4 eV was observed in the middle of 20 nm Ag layer. The plasmons were localized at the metal/dielectric interface for Ag layers 5 nm and less. The reflectance spectral profiles edges positions at long and short waves are correlated with plasmons energies and features of their spatial distribution. The MIMs based on the TiAlN/Ag can find applications as optical filters, photovoltaic energy conversion devices, etc.

1. Introduction

Modern antireflection optical coatings are designed as combinations of dielectrics and metal thin layers. Metal layers are acting through the bulk reflectance and absorption properties of the material. Dielectric thin films are using optical interference. The reflectance and transmittance in these coatings are achieved due to pumping of plasmon oscillations in the multilayer coating by impinging light.

Excitation of plasmons at optical frequencies and coupling them back into freely propagating light are processes of great interest for the manipulation with transmitted and reflected light. Plasmonics involving manipulation of bulk and surface plasmon resonance in a metal allows changing the wavelength and intensity of electromagnetic radiation at its absorption and reemission. These processes are occurring in the metal-dielectric metamaterials with dimensions of structural elements comparable with electromagnetic wavelength. Multilayer designs can deliver higher performance and enable operation over a wider range of wavelengths filtering and focusing electromagnetic waves. Physical properties and electronic structure of a metal and a dielectric in the nanocomposite are controlling energy and intensity of free electrons resonance as well as electromagnetic field localization on interfaces.

Plasmonic structures can manipulate light at a subwavelength scale because large spatial frequency components associated with metallic structures with subwavelength-sharp features [1–3]. The attention to plasmon metamaterials design paid in recent years is stipulated by ideas to apply their exciting optical functions such as field localization, refractive index engineering, phase and amplitude control, and many more [4].

2. Materials and methods

The multilayer $(Ti_{34}Al_{66})N/Ag$ heterostructures with different thicknesses of individual layers (see table 1) and two reference 580 and 1000 nm TiAlN coatings were fabricated by DC-magnetron sputtering. The thicknesses of individual layers were varied from several to several hundred nanometers. All samples were covered with TiAlN layer to protect silver layer from oxidation.

Table 1. Multilayer coatings composition parameters.

Sample	TiAlN layer thickness, nm	Ag layer thickness, nm	TiAlN/Ag bilayers	Total thickness, nm
1	40	40	6	480
2	40	20	8	480
3	20	20	12	480
4	20	10	16	480
5	10	5	33	495

Light reflection measurements (figure 1(a)) were acquired in the total reflection mode (incidence angle 5°) with a Shimadzu UV-VIS-NIR Spectrophotometer SolidSpec-3700. The reference signal was taken from an aluminum coated mirror. One can see that each multilayer coating has its own band of maximal reflection suppression.

To restore the optical constants of MIMs we used the Drude-Lorentz (DL) model and Transfer Matrix Method (TMM) to fit the light reflection experimental data. Such fitting was based on Levenberg-Marquardt algorithm.

According to DL model the complex dielectric function $\varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2$ could be written as:

$$\varepsilon = \varepsilon_\infty - \omega_p^2 \sum_j \frac{f_j}{\omega_j^2 - \omega^2 + i\omega G_j}; \omega_0 = 0, \tag{1}$$

where ω_p is a bulk plasmon frequency, eV; ω – primary light frequency, eV; ω_j – resonant frequency, eV; G_j – dumping coefficient (attenuation time), eV.

The complex refractive index $N = n + ik$ of planar MIM is an important attribute of absorption of light propagating through the film.

Refraction (n) and extinction (k) coefficients were calculated as:

$$n = \sqrt{\frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1}{2}}; \quad k = \sqrt{\frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1}{2}}, \tag{2}$$

The surface reflectivity coefficient was calculated as:

$$R(T_e, T_p, \omega) = ((n-1)^2 + k^2)/((n+1)^2 + k^2). \tag{3}$$

3. Results and discussion

The reflective index $n(\omega)$ can be presented as a function of angular plasmon frequency ω_p, total scattering rates v_m, angular light frequency ω and extinction coefficient k as:

$$n^2 = \frac{1}{2}\left[\left(1 - \frac{\omega_p^2}{\omega^2 + v_m^2}\right)^2 + \left(\frac{v_m}{\omega} \frac{\omega_p^2}{\omega^2 + v_m^2}\right)^2\right]^{\frac{1}{2}} + \frac{1}{2}\left(1 - \frac{\omega_p^2}{\omega^2 + v_m^2}\right), \tag{4}$$

where bulk plasmon frequency ω_p is defined by the material

$$\omega_p = \sqrt{Ne^2/\varepsilon m_{eff}} \ , \tag{5}$$

N, ε, m_{eff} are the density, dielectric permittivity and the effective mass of the conduction electrons, respectively. Influence of the ionic lattice on the conduction electrons can be accounted using the effective electronic mass m_{eff} instead of m_e. According to DL model, the refractive index depends on plasmon frequency.

Features of plasmons energy and spatial distribution in thin Ag layers as well as plasmon-polariton interactions on metal-dielectric interfaces in TiAlN/Ag MIM coatings under study were reported earlier in [5]. There was found that plasmon frequencies are rising while their intensities are attenuating with Ag layer tightening. It is paradoxical because decreasing of plasmons intensities due to density of conduction electrons reduction shall be accompanied by plasmon frequency (i.e. energy) decreasing according to equation (4). The contradiction can be resolved accounting features of electronic structure of silver as a d-element.

The calculated d-screened surface plasmon energy in Ag layer depends on the bulk plasmon energy ω_p in presence of d-electrons characterized by the frequency dependent dielectric function $\varepsilon_d(\omega)$ as [6]:

$$\omega_s = \frac{\omega_p}{\sqrt{1+\varepsilon_d(\omega_s)}} = 3.62 \ eV. \tag{6}$$

Measured plasmon energies were 3.55, 3.45, 3.39 and 3.20 eV for 5, 10, 20 and 40 nm Ag layers, correspondingly [7]. The plasmon energies are bigger in thinner nanolayers because plasmons in thin Ag layer with s- and d-bands crossing the Fermi level are strongly damped by interband transitions. Increased binding energy of the plasmon with ion core (localized $5s$ electrons) provides its bigger excitation energy as we see with Ag layer thinning. The similar growth of the surface plasmon energy at nanostructuring was demonstrated in [8, 9] for silver clusters.

Figure 1(a) demonstrates complex influence of Ag/TiAlN coatings architecture on their reflectance. So, the coating with 40 nm layers of Ag and TiAlN (ML-40/40×06) possesses reflectance more than 30 % in whole investigated band of photon energies. Its antireflectance properties are enough poor.

Figure 1(a) demonstrates also that each multilayer coating has its own band of maximal reflection suppression in region of frequency $\omega_0 = \lambda_0/\hbar c$ corresponding to resonant adsorption by surface plasmon resonance. In the long-wave region at $\omega < \omega_0$ reflectance is growing with ω decreasing, and threshold of reflectance is shifted according to ω_0 variations. The resonance frequency of adsorption goes to longer waves at increasing number of bilayers of same thicknesses.
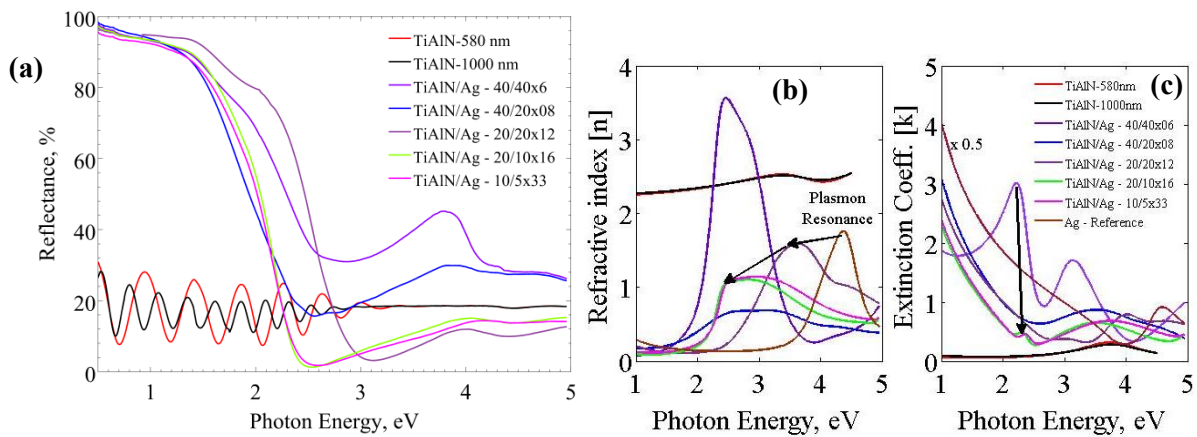

Figure 1. Reflectance spectra of single layer TiAlN (580 and 1000 nm) and TiAlN/Ag coatings **(a)**, refractive index n **(b)** and extinction coefficient k **(c)** of the coatings and bulk Ag calculated by TMM.

It is clearly seen from figure 2(a) that there are at least four characteristic excitations playing an important role in MIMs optical properties formation. The first group is responsible for absorption of electromagnetic waves by plasmons of metallic layers. These plasmons were detected by REELS and attributed as surface plasmons [5]. The energy of this group of excitations increases with individual layers thinning. It means that nanostructuring in MIM should cause the shift of light absorption edge toward IR region. But as we can see in figures 1(b), (c) there are some more features at the n and k dependencies. There is a peak around 2.5 eV for finest architectures (10/5 and 20/10) of the nanocomposite that correspond not only to plasmons excitations but also its further propagation of the plasmon into volume of TiAlN thin layer.
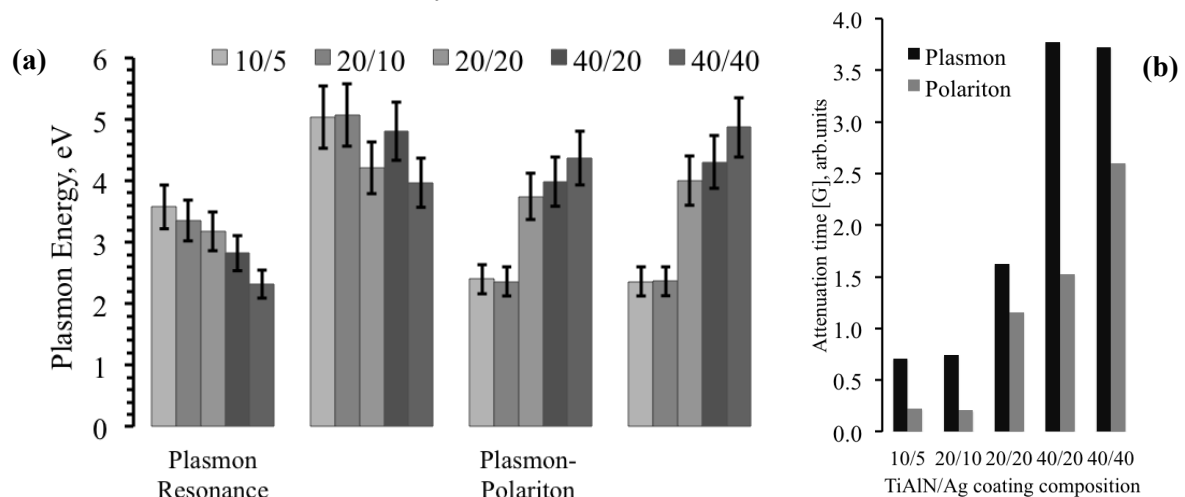

Figure 2. Plasmon resonance in TiAlN/Ag multilayer coatings: resonant frequency **(a)** and damping coefficient (attenuation time) **(b)** for plasmon-polariton excitations.

So, the second group of excitations (figure 2(b)) reflects the plasmon-polariton penetration (PPP) from metallic to insulator layer. Frequencies of plasmons that resonate with Ti 3d or Ag 5s electrons in TiAlN depend on the thicknesses of either insulator or metallic individual layers. Such kind of resonance gives the two absorption edges (e.g. Lorentz terms) with close resonant frequencies ω_t but with significantly different attenuation times G_i. According to our calculations both plasmon and polariton attenuation time (figure 2(b)) is 4–5 times lower for 10/5 and 20/10 samples than for 40/40 one. As attenuation time of excited polariton decreases, the depth of plasmon penetration into nitride layer is decreasing also. The reflection of light in this region (see figure 2(b)) of wavelengths sharply goes down.

So we can conclude that while characteristic size of TiAlN/Ag MIM nanolayers are lower than 20/20 nm, the plasmon-polariton resonance happens to play the prevalent role in optical properties formation instead of plasmon excitation for relatively thick MIM structures.

The results on plasmon losses measured by electron spectroscopy techniques and restored from optical data are in the perfect agreement.

4. Conclusions
Plasmon nanocomposites of Ag/TiAlN system could be applied as broadband optical coatings with high light transmission and low reflection at selected wavelength range of electromagnetic spectrum with practically total reflection of IR radiation and relatively high reflection of UV. We found interrelations between plasmon resonance and light absorption band for MIM nanocomposites with metal layers thickness from 20 to 5 nm. The IR and UV cut-off positions are shifted through the electromagnetic spectrum depending on the plasmonic system parameters determined by thickness and number of layers in the nanolaminate. Basing on these regularities, the reflection and transmission bands of coatings can be tuned by architecture of the plasmonic system varying number and thickness

of dielectric and metal layers as well as their chemical composition. The design of these optical band filters should take also into account the features of polaritonic excitations rising in dielectric layers.

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