Optical properties of thin Ag - In films prepared by interdiffusion in bimetallic nanolayered stacks

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Abstract. The present work reports on the preparation, structural and optical properties of thin bimetallic films from the Ag-In system. Thin films with required compositions were prepared by annealing of Ag/In stacks. The chemical and phase composition, as well as the surface morphology of thin films were analyzed by energy dispersive X-ray microanalysis, X-ray diffraction and atomic force microscopy, respectively. The optical properties of the thin film coatings were characterized by spectroscopic ellipsometry. The increase of the indium content increases the values of the imaginary part of the complex permittivity in the visible spectral region and decreases them in the ultraviolet spectral region. As a result, a shift of the plasmonic activity towards higher photon energies was achieved.

1. Introduction

The interband transitions in gold and silver are the reason for reduction of their plasmonic activity in the ultraviolet spectral range [1]. This straitens the use of the phenomenon of surface plasmon resonance (SPR) in this part of the electromagnetic spectrum, required for a number of applications, such as catalysis and techniques for high-resolution sensing - surface stimulated fluorescence spectroscopy and Raman spectroscopy. Thus, special attention is paid to some poor metals, as Ga, Al, In and Bi [1], despite their low efficiency for excitation of SPR. One way to expand the spectral range is by using alloys of two metals, achieving a variation of the plasmon frequency in the interval between the frequencies of the individual metals. This is the reason, in recent years, for the growing interest in the study of optical properties in solid solutions, such as Ag-Al [2] and Ag-Au [3]. However, only the optical properties of bulk Ag-In alloys with indium content up to 12 at % were investigated in earlier papers [4, 5]. The authors of [6] report decomposition of bulk alloy material Ag75In25 during the process of vacuum film deposition, which causes resultant composition of the thin films of Ag50In50. They observed that the optical absorption is dominated by a strong surface plasmon resonance in the near ultraviolet region for Ag50In50 clusters.

In this work, we demonstrate the possibility to obtain thin films from the Ag-In system with required composition by deposition of multilayered stacks and subsequent annealing. The compositional dependence of the optical properties of thin layers of the Ag-In system was investigated by spectroscopic ellipsometry. The calculated dispersion of real and imaginary part of complex permittivity was used to analyse the plasmonic activity of the investigated materials.
2. Experimental details

Thin films with required compositions were prepared by annealing of Ag/In stacks obtained by thermal evaporation at a pressure of the residual gas of ~ 10^-3 Pa. The Ag/In multilayered coatings, consisted by 17 alternating Ag and In films, were deposited on Si(100) wafer in one vacuum cycle using two independent sources for the evaporation of the two metals. The thicknesses of silver and indium sublayers in the stacks, controlled by quartz monitoring, were chosen to produce thin layers with Ag/In ratio of 20:1, 10:1, 3:1, and 1:2. In the present work, we controlled the mass thickness of the sublayers, which is the thickness of a continuous film with the density of the bulk metal. The mass thickness of the sublayers is given in table 1. The as-deposited multilayered stacks were annealed at 150°C at a residual gas pressure of ~ 10^-3 Pa. The annealing temperature was chosen to be 10°C lower than the melting point of indium.

The chemical compositions of the thin films were determined by X-ray microanalysis using a scanning electron microscope SEM Philips 505 with an EDAX 9100 microanalyzer. X-ray diffraction (XRD) patterns were collected using an X-ray diffractometer "Philips 1710" - with monochromatic CuK\(\alpha\) emission (\(\lambda = 1.54056 \text{ Å}\)).

Atomic Force Microscopy (AFM), MFD-3D Asylum Research (Oxford Instruments), was used to determine the sample topography and surface roughness. For these measurements, standard silicon probes AC 160 TS with frequency of 300 kHz and spring constant of 26 N/m were used. The experiments were carried out in a non-contact AC mode.

The optical properties of the films were examined by a Woollam M2000D spectroscopic ellipsometer in the spectral range of 1.2-6.5 eV at an angle of incidence of 70°. A single layer with a rough overlayer model on an absorbing substrate was applied. In our calculation, we assume that the films possess random roughness and the surface rough layer consist by 50% film material and 50% air. The validity of the model was determined by minimization of the values of mean square error function (\(\chi^2\)), which accounts the discrepancies between the measured spectra of ellipsometric angles \(\Psi_{\text{meas}}\) and \(\Delta_{\text{meas}}\) and theoretical calculated values for \(\Psi_{\text{calc}}\) and \(\Delta_{\text{calc}}\). The \(\chi^2\) values in our calculation were in the range of 0.05 – 5 [7].

3. Results and discussion

The total thickness of the deposition of multilayered stacks was chosen to be of about 200 nanometers in order to avoid the influence of the size effect on the optical parameters. The compositions of the thin films were chosen according to the Ag-In phase diagram. The last can be separated to three regions: region of boundary Ag-based solid solutions in the interval 0–25 at. % In; region of crystalline phases: \(\text{Ag}_x\text{In}_y\), \(\text{Ag}_9\text{In}_4\) (\(\text{Ag}_2\text{In}\)), \(\text{Ag}_2\text{In}_2\) and solid solutions on their base, situated between 25 and 67 at. % In; and bimetallic \(\text{AgIn}_2\)–In alloys at indium content greater than 67 at. % [8]. The results from the X-ray microanalysis of the thin films from Ag-In system after annealing at 150°C are shown in table 1. It is seen that the composition of the coatings is close to the expected one.

| Expected composition (at. %) | Ag mass thickness (nm) | In mass thickness (nm) | Number of sublayers | Realized composition after annealing (at. %) |
|-----------------------------|------------------------|-----------------------|---------------------|-------------------------------------------|
| \(\text{Ag}_{98}\text{In}_2\) (20:1) | 95                     | 2                     | 17                  | \(\text{Ag}_{97.7}\text{In}_{2.3}\)         |
| \(\text{Ag}_{90}\text{In}_{10}\) (10:1) | 9                      | 3                     | 17                  | \(\text{Ag}_{90.0}\text{In}_{10.0}\)        |
| \(\text{Ag}_{75}\text{In}_{25}\) (3:1) | 9                      | 6                     | 17                  | \(\text{Ag}_{75.3}\text{In}_{24.7}\)        |
| \(\text{Ag}_{33}\text{In}_{67}\) (1:2) | 4                      | 15                    | 17                  | \(\text{Ag}_{33.5}\text{In}_{66.5}\)        |
Figure 1. X-ray diffraction patterns of thin films from the Ag-In system before and after annealing at 150°C (annealed films are labeled with (a)).

Figure 2. AFM images of thin films from the Ag-In system: a) Ag98:In2; b) Ag75:In25 and c) Ag33:In67. The corresponding RMS surface roughness is given.

Figure 1 presents the XRD patterns of the investigated thin Ag-In films before and after annealing at 150°C. The positions of the diffraction peaks of the phases indicated in the thin films, according to Ag (JCPDS 87-0720), Ag3In (JCPDS 29-0672), Ag9In4 (JCPDS 29-0678), AgIn2 (JCPDS 25-0386) and In (JCPDS 05-0642), are shown by the corresponding symbols in the figure. The X-ray diffraction patterns of the thin films with In content up to 10 at. % showed presence of silver-based solid solution, defined by a shift of the Ag reflexes towards the indium ones with the increase of the indium content. The presence of a solid solution even in the as-deposited multilayer coatings suggests its formation either by diffusion of the “hot” silver atoms falling on the already deposited thin indium layer or by diffusion of Ag atoms at room temperature after the end of the thin films deposition. Some authors report diffusion of silver in indium even at temperatures of -33°C [9]. Still, some free elemental indium is observed in both as-deposited and annealed coatings, as its quantity decreases after annealing, which is evident from the significant intensity change of the peak belonging to indium on the XRD patterns. The thin Ag98:In2 film is a mixture of Ag3In and Ag9In4 crystals, while in the Ag33:In67 film only presence of the AgIn2 crystalline phase, even before annealing, was indicated.

The AFM images showed that thin films topology of all samples is “grain-like” (figure 2). The size of the grains ranges from 20-50 nm for the thin films with composition Ag98:In2 and Ag90:In10. The Ag75:In25 and Ag33:In67 samples demonstrate significantly larger grains up to 100-160 nm and 700-1000 nm, respectively. The root mean square surface roughness (RMS) increases with increasing the In content in the thin layers from 8.6 nm to 56 nm.
Figure 3. Dispersion of the real and imaginary parts of the complex permittivity of thin Ag-In films before and after annealing at 150°C. The insets present the spectra of $\varepsilon'$ around the cross-over point.

The dispersion of the complex permittivity of the thin Ag-In films was determined using the Drude-Lorentz model (figure 3). This model consists of a Drude part, $\varepsilon_D$, which gives the contribution of free electrons and a Lorentzian-like part, $\varepsilon_L$, related to interband transitions:

$$
\varepsilon = \varepsilon_D + \varepsilon_L = 1 - \frac{\omega_{Dp}^2}{\omega_{Dp}^2 + i \omega \Gamma_p} + \sum_{j=1}^{3} \frac{f_j \omega_{rj}^2}{\omega^2 - i \omega \Gamma_j},
$$

where $\omega_0$ is permittivity at infinite frequency, $\omega_D$ is plasma frequency and $\Gamma_p$ is damping coefficient. The Lorentzian-like parts are characterized with resonance frequencies $\omega_{rj}$, oscillator strengths $f_j$ and damping factors $\Gamma_j$. A minimum of 3 oscillators were required to achieve a good fit between the measured spectra of the ellipsometric angles $\Psi_{\text{meas}}$ and $\Delta_{\text{meas}}$ and the theoretically calculated values of $\Psi_{\text{calc}}$ and $\Delta_{\text{calc}}$. In the case of as-deposited multilayer coatings, the values of $\varepsilon'$ and $\varepsilon''$ are influenced by the indium content.

The real part of the complex permittivity does not depend on the composition of thin Ag-In films with indium content below 25 at. % before the annealing. A decrease of the absolute values of $\varepsilon'$ is observed for the films with 2 and 10 at. % In after the annealing at 150°C, while the thermal treatment does not affect the spectra of $\varepsilon'$ of the thin films with compositions Ag$_{75}$:In$_{25}$ and Ag$_{33}$:In$_{67}$. The obtained position for the cross-over point for $\varepsilon' = 0$, related with the volume plasmon frequencies of silver, is at 3.81 eV, which is in good agreement with the existing literature data [10]. A shift of this point to the higher photon energies - 3.96 eV and 4.08 eV is observed for the thin layers with compositions Ag$_{90}$:In$_{10}$ and Ag$_{90}$:In$_{10}$, respectively. The switch of the sign of $\varepsilon'$ ($= 0$) for the Ag$_{75}$:In$_{25}$ film is at 6.45 eV, while for the Ag$_{33}$:In$_{67}$ film this effect is out of the range of the present...
measurements. A negligible shift of the cross-over point for $\varepsilon' = 0$ within 0.01 - 0.02 eV is observed after annealing of thin films.

The increase of the indium content in the thin films increases the values of the imaginary part, $\varepsilon''$ of the complex permittivity in the visible spectral region and decreases them in the ultraviolet spectral region. No drastic changes were observed in the spectra of $\varepsilon''$ after annealing.

Figure 4. Calculated spectra of the complex permittivity Lorentzian part for annealed Ag-In coatings.

Figure 4 presents calculated spectra of the Lorentzian part of the complex permittivity for annealed Ag-In coatings. It is seen that the increase of indium content shifts the interband transition from $4d$ electronic states of silver and indium atoms to Fermi level in conduction band in the visible spectral range. As a result an anomalous dispersion of the real part of permittivity, $\varepsilon_R'$ is observed for photon energies greater than 3 eV, while the values of the imaginary part of the dielectric function are lower than those of the silver in the same spectral region. Since the real part of the Drude component is always negative at frequencies lower than the plasmon frequency, $\omega_{pl}$, the anomalous dispersion of the Lorentz part will increase the negativity of the values of $\varepsilon'$ in the UV spectral range. This suggests an improvement in the excitation efficiency of localized surface plasmon resonance in the ultraviolet region, defined in the case of spherical particles as a ratio - $Q_{LSPR} = \varepsilon' / \varepsilon''$ [11].

Finally, we examined the obtained results by calculation of the spectra of the cross-section of excitation of spherical Ag-In nanoparticles with diameter, $a = 20$ nm embedded in a dielectric medium with refractive index of 1.5. The numbers in figure indicate the Ag-In nanoparticles’ composition.

Figure 5. Cross-section of excitation spectra of spherical Ag-In nanoparticles with diameter, $a = 20$ nm embedded in a dielectric medium with refractive index 1.5. The numbers in figure indicate the Ag-In nanoparticles’ composition.

The cross-section of extinction is a sum of absorption and scattering. For small particles, the excitation is dominated from the absorption cross-section $- \sigma_{abs} = \frac{k^2}{\varepsilon_0} \text{Im} (\alpha)$, while the larger particles’ main contribution has scattering cross-section $- \sigma_{scattering} = \left( \frac{k^4}{6\pi\varepsilon_0^2} \right) |\alpha|$, where $k = 2\pi/a$ is wave vector, $\varepsilon_0$ is dielectric constant and with $\alpha$ is denoted the polarizability of a sphere.
\[
\alpha = 4\pi\varepsilon_0\alpha^3 \frac{\varepsilon(h\omega) - \varepsilon_m}{\varepsilon(h\omega) + \varepsilon_m},
\]

where \(\varepsilon(h\omega)\) and \(\varepsilon_m\) are the complex permittivities of the Ag-In nanoparticles and the surrounding media, respectively. The open symbols in the inset of figure 5 show the literature data for the excitation spectra of Ag, In and Ag\(_{50}\)In\(_{50}\) clusters [6, 13-14] and the dash line presents the obtained compositional dependence of the position of the excitation maximum. The delivered data suggest that the increasing of indium content in thin films from Ag-In system shifts the excitation maximum in the ultraviolet spectral range from 3.01 eV for Ag nanoparticles to 5.23 eV for nanoparticles with composition Ag\(_{33}\):In\(_{67}\). The lower efficiencies are due to the higher values of the imaginary part, \(\varepsilon''\) in the UV region in comparison with those of the silver in the visible spectral range.

4. Conclusions

The present work reports on the preparation, structural and optical properties of thin bimetallic films from the Ag-In system prepared by annealing of Ag/In stacks. The X-ray diffraction results showed that the phase composition of the thin films corresponds well to that of the Ag-In phase diagram. The dispersion of the complex permittivity, determined by ellipsometric measurements, suggests the possibility of excitation and tuning of the localized surface plasmon resonance to a certain frequency in the UV spectral range from 3 to 6 eV by varying the film’s composition. Based on the analysis of the Lorentz part of the complex permittivity, the contribution of the interband transitions to the improvement of the plasmon activity in the ultraviolet region has been established. The simulated spectra of the cross-section of excitation of spherical nanoparticles shows shifts of the excitation maximum in the ultraviolet spectral range from 3.01 eV for Ag nanoparticles to 5.23 eV for nanoparticles with composition Ag\(_{33}\):In\(_{67}\).

Acknowledgments

This work is financially supported by contract KP-06-N38/8 - 05.12.2019 with the Bulgarian National Science Fund (BNSF).

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