Preparation and optical characterization of Au – In films for plasmonic applications

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Abstract. Thin Au-In films were prepared by thermal co-evaporation and studied by the means of energy dispersive X-ray analysis, X-ray diffraction, scanning electron microscopy and spectroscopic ellipsometry. The alloying tendency in the as-deposited thin films was analysed and the influence of the AuIn2 and Au7In3 compounds on the optical properties and the possibility for excitation of a plasmon resonance in the bimetallic condensates was analysed.

1. Introduction
The research and development of precise approaches for detection of small quantities of specimens became of even greater importance in the sense of the ongoing COVID-19 pandemic. The surface enhanced Raman spectroscopy (SERS) and the plasmon-enhanced ultra-violet fluorescence are powerful tools for analysis and determination of small amounts of organic molecules [1]. It has been already proven that a coating of silver or gold on the SERS template causes a significant amplification of the detected Raman signal from the investigated substance, due to the presence of plasmon resonance in the metals [2]. In this sense, the development of new materials and structures with optical response in such spectral regions of interest is a state-of-art topic.

The excitement of plasmons with high enough intensity at a desired energy band is usually realized either by confinement of the metallic particle’s dimensions or by a combination of two materials possessing the desired electronic structures for excitement of plasmons [3,4]. The first approach is proven to be good but it requires either additional processing or the usage of a limited number of materials whose crystalline structure allows a directed growth. The second method is based on tuning of the desired property by determination of a proper ratio between the two consisting materials. Its advantages are based on the possibility for preparation of a plasmonic material in one cycle without further processing and with no need of extremely precise preparation conditions, because the plasmonic effect is caused only by electronic interaction between the two metals.

The metals, such as Al, Ga, In, Sn, Tl, Pb, and Bi, despite their relatively low efficiency, are potential candidates for the plasmonic applications in the near to far ultraviolet spectral range (3.1 – 12.0 eV), similarly to silver and gold in the visible spectral range [5]. In this order, to achieve adjustment of the plasma frequency and to improve their plasmonic activity, the alloys of indium with gold and/or silver are attractive materials for UV plasmonics.

In this work we discuss the preparation and the optical investigation of thin films from the Au-In system deposited by thermal co-evaporation.
2. Experimental

Thin films were prepared by thermal co-evaporation of Au and In on Si wafers in estimated ratios of interest conformed with the specifics of the Au-In phase diagram [6]. The deposition of the samples was made under vacuum of $\sim 10^{-3}$ Pa and the compositions were realized through variation of the deposition rates of the two elements. The nominal thickness (quantity of deposited material) of the films, as well as the deposition rate of the elements were monitored throughout the whole process by a quartz crystal microbalance device. All samples’ nominal thicknesses were set to be 200 nm.

The resultant composition of the samples was determined by energy dispersive X-ray microanalysis using a scanning electron microscope SEM Philips 505 with an EDAX 9100 microanalyzer, and the surface morphology was observed by SEM (accelerating voltage 8 kV, magnification of 20 000x).

The phase composition of the Au-In films was revealed through the means of X-ray diffraction (XRD). The XRD patterns were taken using an X-ray diffractometer Philips 1710 with CuK$_\alpha$ irradiation ($\lambda = 0.15406$ nm) in the Bragg angles ($2\theta$) range from 30 to 60° (step of 0.03°).

The optical properties were further evaluated by spectroscopic ellipsometry. The ellipsometric measurements were performed in the spectral range of 1.2-6.5 eV using a Woollam M-2000D spectroscopic ellipsometer at an angle of incidence of 70°. The dispersion of the complex dielectric permittivity of the thin Au-In alloys was determined using the Drude-Lorentz model [7] in a modelled optical structure of thin continuous layer with surface roughness on top on an absorbing substrate, whose validity was determined by calculation of a common mean square error function ($\chi^2$), which accounts for the discrepancies between the measured and simulated data [8].

3. Results and discussion

The samples’ compositions were chosen, according the Au-In phase diagram [6], to be situated in the Au-rich region of solid solutions; near the AuIn$_2$ compound; and in the In-rich region of AuIn$_2$-In mixtures. The estimated and resultant (determined by X-ray microanalysis) compositions of the samples, as well as the deposition rate ratios used for their realization are presented in Table 1.

Table 1. Expected and resultant composition of thin Au-In films, deposition rate ratio of the initial elements. Optical properties of the as-deposited films – plasma frequency ($\omega_{Dp}$) and damping coefficient of free electron ($\Gamma_D$), calculated by spectroscopic ellipsometry.

| Estimated composition | Resultant composition | Deposition rate ratio (Au:In) | $\omega_{Dp}$ [eV] | $\Gamma_D$ [eV] |
|-----------------------|-----------------------|-------------------------------|-----------------|----------------|
| Au                    | Au100                 | -                             | 9.2             | 0.18           |
| Au85:In15            | Au84:In16             | 10.0:1.0                      | 15.1            | 0.35           |
| Au25:In75            | Au22:In78             | 1.0:1.5                       | 8.24            | 0.06           |
| Au2:In98             | Au2:In98              | 1.0:30.0                      | 5.29            | 0.75           |
| In                    | In100                 | -                             | 11.2            | 0.20           |

The phase analysis of the XRD patterns (figure 1) showed significant alloying of the initial elements with a good correspondence to the compositional peculiarities of the Au-In phase diagram. The diffraction pattern of the thin Au film (figure 1a) corresponds to an elemental gold (JCPDS 04-0784). A peak from the Si substrate appears at $2\theta = 33^\circ$ with a shoulder at 32.5°, as the last can be associated to both substrate fluctuations or presence of a certain amount of AuO (JCPDS 23-0278, $2\theta = 32.57^\circ$). However, the first seems to be more accurate because no AuO peaks were registered on the other XRD patterns. The Au-rich sample appears to be composed by a Au-In$_3$-based solid solution (Au-In$_3$; JCPDS 29-0647) and probably some amount of elemental gold (figure 1b). The Au$_{22}$:In$_{78}$ sample is consisted predominantly by the AuIn$_2$ phase (JCPDS 03-0339) and a residual indium (figure 1c), which is in good agreement with the elemental analysis. A single peak with high intensity was registered in the In-rich sample with 2 % Au doping, which corresponds to the main peak of the
indium pattern (JCPDS 05-0642) with a slight deviation from its stable position, most probably related to a lattice strain caused by the gold additive.

The diffraction pattern of the Au$_{84}$:In$_{16}$ sample (figure 1b) reveals a wide X-ray amorphous plateau covering the characteristic effects of the Au:In compound. Since neither the preparation method, nor the materials used suggest probability of formation of an amorphous structure, this effect may be associated to formation of extremely small disordered nanocrystals. This assumption was confirmed to a certain degree by the SEM observations – the surface seems homogeneous and smooth (figure 2b), but more profound investigations of this composition would be of certain interest. The Au$_{22}$:In$_{78}$ sample is also smooth with a number of randomly distributed inclusions, which may be associated to the residual indium. The further addition of indium leads to appearance of well-defined grains with dimensions of above 1 μm – figure 2c.

The complex dielectric permittivity, $\varepsilon$ was determined by ellipsometric measurements in the spectral range of 1.2 - 6.5 eV (figure 3). According to the Drude-Lorentz model, $\varepsilon$ is presented as a sum from a Drude part, $\varepsilon_D$ which gives the contribution of free electrons and a Lorentzian-like part, $\varepsilon_L$ related to interband transitions:

$$\varepsilon = \varepsilon_D + \varepsilon_L = \varepsilon_{\infty} - \frac{\omega_{Dp}^2}{\omega_{Dp}^2 + i\omega\Gamma_D} + \sum_{j=1}^{n} \frac{f_j\omega_j^2}{\omega_j^2 + i\omega\Gamma_j},$$  

where $\varepsilon_{\infty}$ is the dielectric permittivity at infinite frequency, $\omega_{Dp}$ is plasma frequency and $\Gamma_D$ is damping coefficient of a free electron. The calculated values of the parameters from the Drude part are given in table 1. The dispersions of the real and imaginary parts of $\varepsilon_D$ are given as insets in figure 3a and b, respectively. The Lorentzian-like parts are characterized with resonance frequencies $\omega_{ij}$, oscillator strengths $f_j$ and damping factors $\Gamma_j$. In the presented work a minimum number of Lorentzian oscillators giving a reasonable agreement between the experimental and calculated spectra was used.

The dielectric permittivity spectrum of the Au film is characterized by a local maximum at ~ 2.5 eV in the $\varepsilon'$ part and a minimum in the $\varepsilon''$ part at ~ 2.1 eV due to the interband transition from 5$d$ states to Fermi level in the conductive band. Taking into account that the $|\varepsilon_D'|$ and $\varepsilon_D''$ are proportional to the free electrons concentration and that the In possesses higher free electron density – 11.5×10$^{28}$ m$^{-3}$ (3 free electrons per atom from the 3s and 3p orbitals) than the Au – 5.90×10$^{28}$ m$^{-3}$ (a single electron from the 6s orbital) [9], would explain the position of the dispersion curves of the Drude components in Au$_{84}$:In$_{16}$ between those of pure Au and In. In this case, the results show that the In additive to the gold decreases the values of $\varepsilon'$ in the spectral range of 2 - 3 eV. The calculated spectra of $\varepsilon_D'$ and $\varepsilon_D''$ for the same Au$_{84}$:In$_{16}$ film show a shift of the interband transitions maximum to the infrared spectral range.

The analysis of the Au$_{22}$:In$_{78}$ and Au$_{2}$:In$_{98}$ films shows a maximum of $\varepsilon'$ at photon energies of 1.8 – 1.9 eV, while the imaginary $\varepsilon''$ part is characterized by a maximum within 2.08 - 2.3 eV, which shifts to the higher energies with the increase of the In content. According to [10] an interband transition is
observed in AuIn$_2$ crystals at ~ 1.8 eV, expressed by maxima in both $\varepsilon'$ and $\varepsilon''$ spectra at 1.8 and 2.1 eV, respectively. A strong interband transition of In is reported at 1.4 eV [11]. As can be seen in figure 3d the overlap of the contribution from the interband transition in In and AuIn$_2$ crystals leads to increase of the real part of complex dielectric permittivity of thin film with composition Au$_{22}$:In$_{78}$.

The plasmon resonance can be identified as a maximum in the optical loss function of the samples: $\text{Im}\{-1/\varepsilon\} = \varepsilon' / (\varepsilon'^2 + \varepsilon''^2)$. The loss function spectra (figure 4) indicate that the plasmonic activity is affected differently by the predominant presence of In or the AuIn$_2$ compound. It is seen that the maximum in the loss-function of the Au$_{22}$:In$_{78}$ film is shifted to the lower photon energy in comparison even to this of the referent Au layer, which might be due to a particular plasmon activity band of the AuIn$_2$ compound. On the other hand, the doping of an indium material with just 2 at. % AuIn$_2$ causes a shift to deeper ultraviolet spectral bands compared to the pure indium reference.

On the other side of the binary diagram, the formation of an Au-rich solid solution based on the Au$_7$In$_3$ compound worsens the plasmonic performance compared to the pure gold reference, which may be caused by either the formation of the compound or because of an undesired size-effect due to the fine granular structure of the layer suggested by the XRD and SEM investigations. Therefore, a further investigation would be of certain interest.

Taking into account the results presented above, it can be stated that the optical performance of the as-deposited films corresponds to the compositional peculiarities of the Au-In phase diagram – the bands of the plasmonic effects are influenced not only by the initial elements, but also by the formed chemical compounds.
4. Conclusions
Thin films from the Au-In system were prepared by alloying of Au and In in gas phase using a thermal co-evaporation approach. The phase and morphological changes in the as-prepared samples were evaluated in the means of chemical composition according to the Au-In phase diagram. The influence of elemental indium and AuIn$_2$ compound on the films’ optical properties were studied. It has been determined that the optical performance of the as-deposited samples is influenced by the phase peculiarities of the realized Au-In alloys and compounds. The predominant presence of AuIn$_2$ compound in the films causes appearance of plasmon activity in the infrared part of the spectrum, while the doping of pure indium with this compound shifts the optical effect even further in the UV. The last observation suggests a possibility for tuning of plasmon excitation bands in the UV spectrum and it would be of practical interest more precise investigations to be performed on the binary AuIn$_2$-In alloys.

Acknowledgement
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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