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Electronic structure and functionalization of Ag-In nanostructures with tryptophan for surface-enhancement spectroscopic application

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INTRODUCTION & AIM

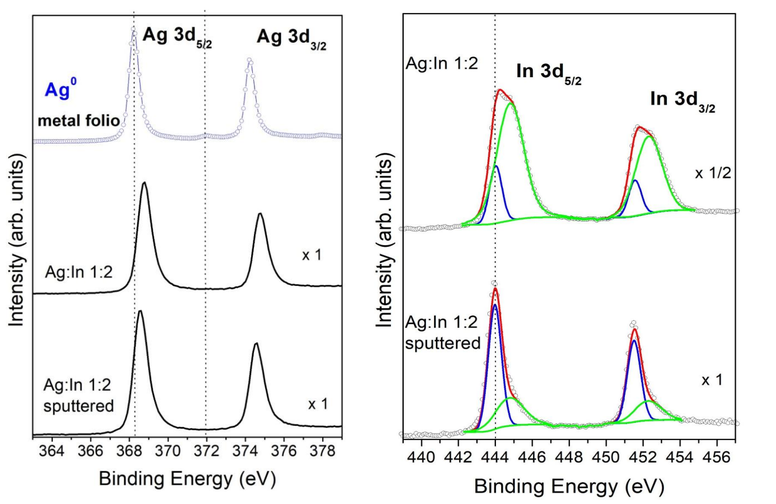
Two major types of interaction of a molecule with a plasmonic nanostructure may cause enhancement of Raman signal: electromagnetic enhancement, in which large local fields are created by electromagnetic resonances occurring near the metal surface, and charge-transfer effect (chemical enhancement), in which the molecular polarizability is affected by the interaction between the studied molecule and the metal surface.

The electronic structure of the materials forming the nanostructure plays a key role during the chemical enhancement. It determines the excitation energy of the non-equilibrium charge carriers (hot electrons and holes) and their interaction with various functional groups of the organic molecules under investigation [1,2].

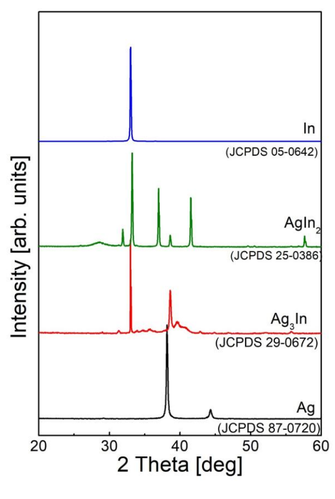
In the present work we discuss the interaction of aqueous solution of tryptophan with thin polycrystalline films of the intermetallic compounds Ag_3In and $AgIn_2$. Thin films with required compositions (Ag/In ratio of 3:1 and 1:2) were prepared by layer-by-layer deposition of alternating very thin films of silver and indium in one vacuum cycle, and the compounds were formed by a self-occurring solid-state reaction. The chemical and phase composition of the thin films, analyzed by energy dispersive X-ray microanalysis and X-ray diffraction, confirmed the formation of the Ag_3In and $AgIn_2$ intermetallic compounds.

METHOD

- The Ag/In multilayered coatings, consisted of 17 alternating Ag and In films, were deposited 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 3:1, and 1:2, corresponding to the Ag_3In and $AgIn_2$ compounds [1, 2].
- The as-deposited multilayered stacks were annealed at 150°C at a residual gas pressure of ~ 10^{-3} Pa at annealing temperature 10°C lower than the In melting point .
- The chemical compositions of the thin Ag-In films were confirmed by X-ray microanalysis using a scanning electron microscope SEM Philips 505 with an EDAX 9100 microanalyzer and X-ray photoelectron spectroscopy (XPS).
- The phase composition was analyzed by X-ray diffraction (XRD), using an X-ray diffractometer "Philips 1710" - with monochromatic CuK_α emission (λ = 1.54056 Å), and the presence of the Ag_3In and $AgIn_2$ phases in the corresponding $Ag_{75}In_{25}$ and $Ag_{67}In_{33}$ thin films was proven.

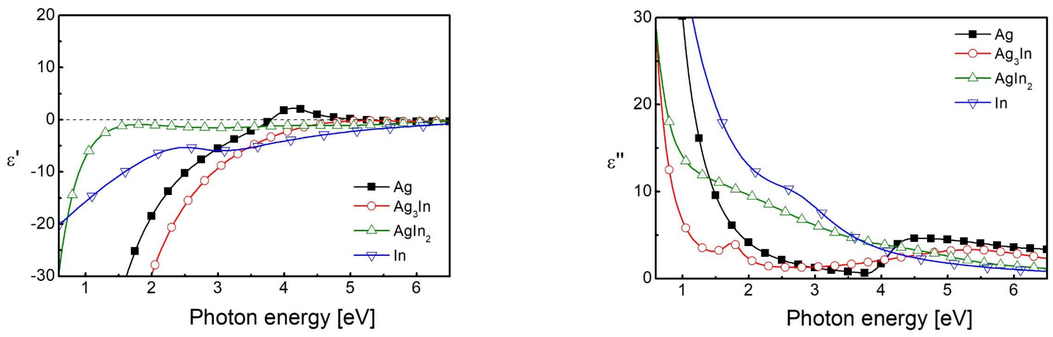


XPS spectra of 3d Ag and 4 d In bands



XRD patterns

- **The optical properties of the films were examined by a UVISEL 2 spectroscopic ellipsometer in the spectral range of 0.6-6.5 eV at an angles of incidence of 50°, 60° and 70°. A single layer with a rough overlayer model on an absorbing substrate was applied.**



Dispersion of the real (a) and imaginary (b) parts of the complex permittivity of Ag-In coatings

- **The Raman spectra were obtained by an USB4000 Ocean Optics spectrometer at 90° scattering geometry, using a 488.0 nm (2.54 eV) line of an argon-ion laser with intensity 60 mW/cm² for excitation. The analyzed samples were prepared using thin metallic or intermetallic films as substrate and one drop of approximately 0.5 mL of 10^{-8} % L-Tryptophan water solutions [2].**

RESULTS & DISCUSSION

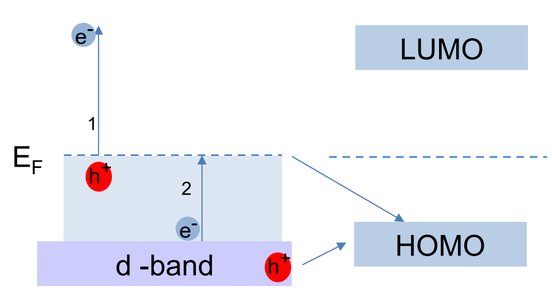
The Surface-Enhanced Raman Scattering (SERS) primarily amplifies molecular vibrations that are aligned parallel to the electric field vector of the localized surface plasmon resonance. The results show a change of the L-Tryptophan (Trp) molecule orientation depending on the composition of the SERS substrate.

- When Ag and Ag_3In substrates were used, an enhancement of the in-plane vibrational modes of NH_3 (1055 cm^{-1} [3]) and CH_2 (1306 cm^{-1} [3]) groups is seen, while an enhancement of their out-plane modes - NH_3 (1133 cm^{-1} [3]) and CH_2 (990 and 1278 cm^{-1} [3]), occurs when a $AgIn_2$ substrate was used, as well as enhancement of the peaks caused by the Trp's pyrrole and indole rings (at 1093, 1229, 1447 and 1490 cm^{-1} [3]).
- When indium was used as a SERS substrate, the Raman scattering at 1388 cm^{-1} [3] decreases because the In 4d band is situated far under the Fermi level and no interband transitions occur.

The chemical interaction of the NH^{3+} and COO^- groups of Trp is determined by the excited electrons and holes in the enhancing material. The excitation of hot electrons occurs by LSPR and interband transitions.

The ellipsometric measurements show :

- In real part of the complex permittivity, the plasma frequency increases to 3.8, 6.9 and 7.0 eV for the Ag, Ag_3In and $AgIn_2$ coatings, respectively.
- The intersection where **ε'** > -2 and fulfils the condition for excitation of LSPR shifts in the UV spectral region in the case **of Ag_3In (4.55 eV) и $AgIn_2$ (5.3 eV) and In (5.2 eV)**



1. Intraband transitions

1(a). Excitation of hot electrons from the Fermi level, which can transition to the antibonding (LUMO) orbitals.

1(b). Low-energetic thermal holes on the Fermi level.

2. Interband transitions

2(a). Excitation of thermal electrons from the d-band to the Fermi level.

2(b). Hot holes in the d-band, which are less mobile and part of them can pass to the bonding (HOMO) orbitals by heterotransition.

CONCLUSION

- The increase of the indium content increases the plasma frequency and the energy for interband transitions.
- The SERS spectra show that the L-Tryptophan orientation depends on the composition of the substrate.
- The variation of the energies of different electronic transitions depending on the composition of the Ag-In coatings can be used for control of the bonding of NH^{3+} and COO^- groups from various amino acids with the materials of the SERS substrate.

FUTURE WORK / REFERENCES

[1]. Todorov, R. and Hristova-Vasileva, T., 2025. Simplified biochemical analysis using p-block metals and their compounds with silver– surface enhancement from the point of view of electronic structure. *ACS Omega*, 10, 19, 19243–19255.

[2]. Todorov, R., Hristova-Vasileva, T., Katrova, V. and Atanasova, A., 2023. Silver and gold containing compounds of p-block elements as perspective materials for UV plasmonics. *ACS Omega*, *8*, 16, 14321-14341.

[3]. Chuang, C.H. and Chen, Y.T., 2009. Raman scattering of L-tryptophan enhanced by surface plasmon of silver nanoparticles: vibrational assignment and structural determination. *J. Raman Spectrosc*, *40*, 150-156.