Laser-driven surface modification of As_2S_3 nanolayers: *in-situ* synchrotron radiation photoemission, surface-enhanced Raman and DFT study

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Laser and thermal assisted transformations of ultrathin (~ 10 nm) As_2S_3 chalcogenide nanolayers were investigated *in-situ* using surface sensitive synchrotron radiation photoelectron spectroscopy. Surface transformations and bond rearrangements were observed both in thermally annealed and laser irradiated samples in comparisons with as-deposited nanolayers. The type of changes were found to be dependent on laser photon energy used for irradiation. In contrast with thermal annealing, the irradiation of As_2S_3 chalcogenide nanolayers by laser operating at 403 nm leads to increase the concentration of As at the surface (compositional changes). Simultaneously, the changes of relative contribution of the As and S atoms occupied different chemical states in whole As *3d* and S *2p* signal were observed. Also, the photo-chemical transformation is found to be reversible in several "laser irradiation – thermal annealing" cycles.

To access the total spectral behavior and to elucidate the structural origin of the chalcogenide surface transformations, the As *3d* and S *2p* core level spectra were fitted using different As- and S-centered structural units (*s. u.*) and their binding energy positions were calculated using *ab initio* DFT method [1]. Surface-enhanced Raman spectroscopy have been also employed for *ex-situ* characterization and study of molecular level details of the laser induced structural transformations occurred at the surface of As_2S_3 nanolayers.

1. *Kondrat O., Holomb R., Popovich N., Mitsa V., Veres M., Csik A., Tsud N., Matoln V., Prince K. C.* Local surface structure and structural properties of As-Se nanolayers studied by synchrotron radiation photoelectron spectroscopy and DFT calculations // J. Non-Cryst. Sol., 2015. – **410**. – P. 180–185.

Photo-degradation processes and thermoconductivity in technologically modified g-As_2S_3 with nanosize inclusions

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Recently by macro FT-Raman and energy-dependent micro-Raman spectroscopy we found the light-induced structural changes in glassy As-S system with realgar As_4S_4 inclusion [1]. Being initially in the structure of glassy closed and connected with glassy network only by weak Van der Vaals forces α (β)-As_4S_4 molecules are transformed into pararealgar p-As_4S_4 form during laser illumination. The effectiveness of transformations depends mainly from photon energies used for irradiation but transformation tendency observed for all used photon energies ranged from 1,65 to 2,54 eV. Our finding is multidisciplinary. It together with another following publication to describe photo-degradation processes in pigment was used since antiquity. The red color of the pigment based on realgar α-As_4S_4 on exposure to light transformed to pararealgar p-As_4S_4 that exhibits yellow color. So light, necessary for viewing a work of art can damage the artwork. Process of light induces polymorph transformation on air is accompanies with formation arsenolite As_2O_3. The process is not completely clarified so far. Based on SRPS and surface enhance Raman spectroscopy studies we found new photo-aged processes occurring on the surface of amorphous As_2S_3 nanosize films for chalcogenide photonics. In energy dependent luminescence in films and glassy As-S with realgar inclusion we have found new evidence not only arsenolite formation but found PL band typical for substance known in general formula $As_2O_3 \cdot H_2O$.

Influence of realgar inclusion on thermal properties photodegradation of glassy As_2S_3 prepared in different technological regime was found. With increasing of melt temperature and the rate of quenching the content of realgar in g-As_2S_3 is increasing what is accompanied with increasing photoaging and decreasing of thermal conductivity from 0,25 to 0,23 (W/Km).

1. *R. Holomb, N. Mateleshko, V. Mitsa, P. Johansson, A. Matic, M. Veres.* New evidence of light-induced structural changes detected in As–S glasses by photon energy dependent Raman spectroscopy // J. Non-Cryst. Sol., 2006. – **352**. – P. 1607–1610.