Nanocomposites and nanomaterials

Micro-Raman evidence of photostructural transformations in Zn-doped As_2Se_3 thin films

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Amorphous arsenic chalcogenide films are well-known photosensitive materials used as optical information storage media, efficient holographic gratings, optical diffraction elements, etc. They often undergo photostructural changes on the nanoscale which can be efficiently studied by Raman spectroscopy.

Here we report on a micro-Raman scattering study of Zn-doped As_2Se_3 thin films grown by a thermal evaporation technique. Measurements were performed at room temperature using a Kr^+ laser (568.2, 647.1, and 676.4 nm lines) and a Dilor XY 800 spectrometer equipped with a CCD camera.

For As_2Se_3 films with a low Zn concentration (0.7 to 5 %) the observed Raman spectra basically reproduce the one of undoped As_2Se_3 films with a dominating broad feature centered near 225 cm^{-1}. For more heavily Zn-doped (7 to 10 %) films, however, the Raman spectra resemble those of the undoped amorphous As_2Se_3 only at low laser power densities P_{exc} while at increasing P_{exc} new sharper features near 200 and 250 cm^{-1} appear. The higher the content of Zn and the shorter the excitation wavelength λ_{exc}, the lower is the power density threshold corresponding to the onset of the changes revealed in the Raman spectra. The distribution of the band intensities, their exact frequency positions and bandwidths depend on the Zn concentration as well as λ_{exc} and P_{exc}.

In most cases the observed new features appear in the Raman spectra of Zn-doped As_2Se_3 film within the acquisition time of 1 min, hence the local photostructural changes in the film are quite fast. These changes are irreversible since the corresponding bands do not disappear after the excitation power is reduced back. Possible reasons for the observed changes are discussed, including the photoinduced formation of either As_4Se_4 structural groups (205 cm^{-1}) and Se_8 rings (252 cm^{-1}) resulting from the rearrangement of the near-order in the glass network, or ZnSe nanocrystallites (205 and 250 cm^{-1}) in the laser spot area.