IN SITU RAMAN STUDIES OF LASER-INDUCED TRANSFORMATIONS IN Cd-DOPED As_2Se_3 FILMS

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Amorphous As_2Se_3 is a semiconductor material with numerous possible applications related mostly to reversible or irreversible photoinduced effects. Contrary to the extensively investigated amorphous As–Se systems with different As and Se content ratio, studies of doped As_2Se_3, except for the Ge–As–Se systems, are rather rare. Here we report on a study of thin As_2Se_3:Cd films grown by a thermal evaporation technique using atomic force microscopy (AFM), energy-dispersive X-ray spectroscopy (EDX), and micro-Raman spectroscopy.

Thin (1–2 μm) Cd-doped As_2Se_3 films with nominal Cd content of 1 to 10% were grown by thermal evaporation on silicate glass and Si substrates. AFM studies (Agilent AFM 5420) reveal a uniform film surface with a roughness of 0.4–0.8 nm.

EDX measurements (NovaSEM microscope) performed at different electron energies (5–30 keV) show that the content of cadmium gradually decreases from the surface into the film depth. For instance, for As_2Se_3 film with nominal 10 % Cd the cadmium content in the surface layer is 18 %, decreasing down to 2.5 % with probing deeper into the film.

Micro-Raman measurements performed at 295 K using a LabRAM spectrometer and a λ_{exc}=514.7 nm or a λ_{exc}=632.8 nm laser show that at low laser power densities P_{exc} the observed Raman spectra of the Cd-doped films basically reproduce that of the undoped As_2Se_3 films with a dominating broad feature near 225 cm^{-1} that is a clear evidence of their amorphous structure. With increasing P_{exc} a new sharp peak appears at 204–209 cm^{-1} as well as a smaller maximum near 410–420 cm^{-1}. The new peak positions and intensities depend on the Cd content, P_{exc}, and λ_{exc}.

The new peaks in the As_2Se_3:Cd film Raman spectra appear, as a rule, within an acquisition time below 1 min, meaning that the local photostructural changes in the film are quite fast. At relatively low P_{exc} the evolution of the new Raman features with the illumination time can be traced. These changes are irreversible: the new peaks do not disappear after the excitation power is lowered again. This can be explained by the formation of CdSe nanocrystals in the laser spot area: the corresponding LO and 2LO phonon frequencies for CdSe are 210 and 420 cm^{-1}, respectively. The bands are observed in the As_2Se_3:Cd film spectra at slightly lower frequencies because of tensile strain undergone by the nanocrystals due to a photoplastic effect (radial mass transfer from the laser spot) in the films.

Keywords: amorphous thin films; nanocrystals; Raman scattering