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CdS nanocrystals formed in amorphous GeS_2:Cd films by photoenhanced diffusion

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INTRODUCTION

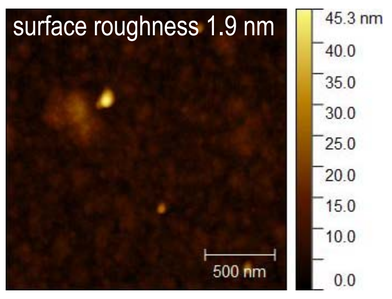
II–VI semiconductor nanocrystals (NCs), in particular CdS, belong to the most widely studied materials of this class produced by colloidal synthesis [1,2], diffusion-limited growth in glass matrices [3], Langmuir-Blodgett technique [4], sequential ion implantation [5] etc. These techniques enable one to obtain ensembles of NCs dispersed in a liquid or an amorphous dielectric matrix. Here we report on a localised formation of CdS NCs in Cd-doped amorphous GeS_2 films due to a strong enhancement of diffusion in the amorphous film induced by bandgap laser light illumination. A similar technique was used to obtain CdS NCs in amorphous As_2S_3 [6] as well as other II–VI NCs in non-crystalline arsenic chalcogenides [7–9].

EXPERIMENTAL

1–2 мм thick Cd-doped (the nominal Cd content up to 10 at.%) GeS_2 films were grown by thermal evaporation technique on silicate glass and silicon substrates. The film surface morphology was checked by Agilent AFM 5420 operating in intermittent contact mode
Micro-Raman measurements were performed at room temperature using a Horiba LabRAM spectrometer with a CCD camera. The excitation was provided by a Cobold Fandango solid-state laser (514.7 nm). The instrumental resolution was in all cases better than 2.5 cm^{-1}.

RESULTS AND DISCUSSION

ATOMIC FORCE MICROSCOPY



AFM studies have shown that the fabricated Cd-doped GeS_2 films are homogeneous with average surface roughness of about 2 nm, slightly increasing with nominal Cd content.

Fig. 1. AFM surface topography of a GeS_2 film

RAMAN SPECTROSCOPY

The reason for the pit formation on the GeS_2 film surface is a drastic non-thermal photoinduced drop of the film viscosity (photosoftening) resulting in a radial mass transfer from the laser spot. Similar effects were observed for As_2S_3 [6, 9] and As_2Se_3 [7–9]. .

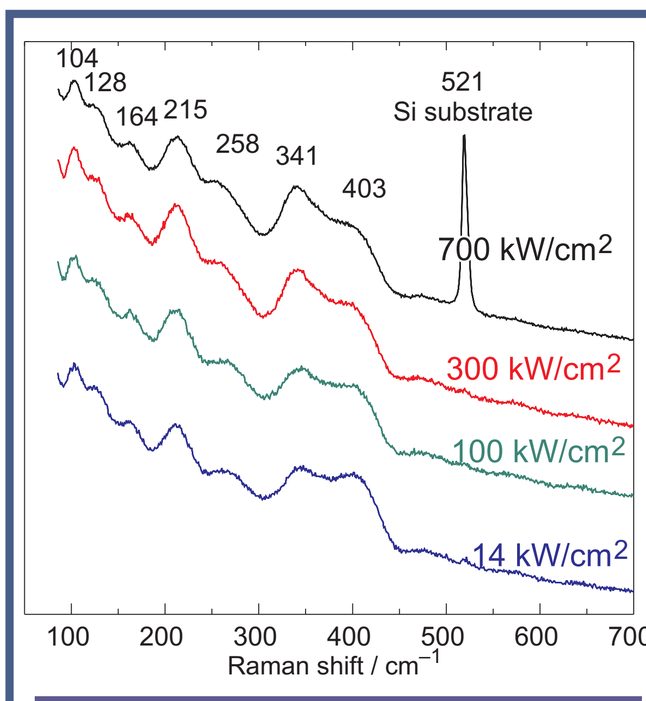


Fig. 2. Raman spectra of an undoped GeS_2 film.

Raman spectra of GeS_2 films exhibit a series of broad features in the interval 100–500 cm^{-1}, typical for amorphous GeS_2 [10]. The spectra do not vary with the laser power density P_{exc}. The peak at 521 cm^{-1} from the silicon substrate appears at the highest because at such P_{exc} a pit is formed on the film surface.

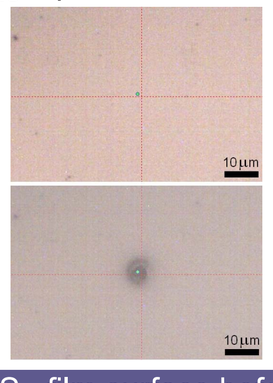


Fig. 3. GeS_2 film surface before and after illumination (700 kW/cm^2, 20 s).

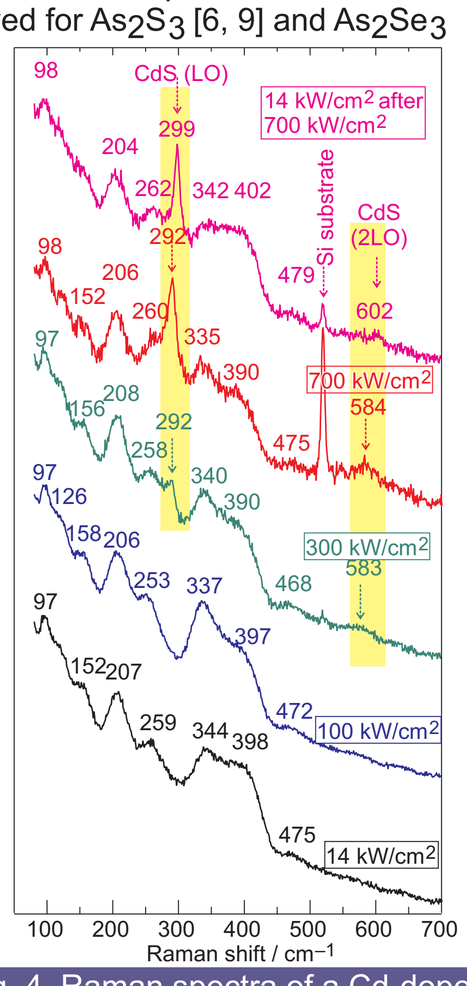


Fig. 4. Raman spectra of a Cd-doped (10 at. %) GeS_2 film at different P_{exc}.

For **Cd-doped** (10 %) GeS_2 films the Raman spectra depend on P_{exc}. At low P_{exc} they are similar to the undoped films (typical amorphous GeS_2). At high P_{exc} suddenly a sharp peak slightly below 300 cm^{-1} and a weaker and broader band at a doubled frequency emerge (highlighted in Fig. 4 by yellow bars). Moreover, the peaks remain after P_{exc} is reduced again showing that the transformation was irreversible.

We relate these peaks to LO and 2LO phonons of CdS NCs formed in the GeS_2 film due to a strong ehnancement of diffusion (photosoftening) enabling Cd and S atoms to assemble in NCs similarly to how it is known for Cd- doped As_2S_3 [6] and As_2Se_3 [7,8].

The CdS LO and 2LO frequencies are below then expected for bulk CdS. This can be related to phonon confinement [11], strain [11], or flexoelectric effect [8]. The first factor is excluded because of a too high downward shift, the role of two others is discussed.

CONCLUSIONS

❶ Good-quality amorphous fims of GeS_2:Cd with surface roughness below 2 nm were obtained by thermal evaporation.
❷ At Pexc > 300 mW/cm^2 a dip is formed in the film surface due to a drastic non-thermal photosoftening of the film and mass transfer from the laser spot.
❸ With increasing P_{exc} for Cd-doped films, CdS NCs are formed due to photoenhanced diffusion.
❹ The observed downward shift of the CdS NC LO and 2LO phonon frequencies can be explained by tensile strain and/or flexoelectric effect.

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