

## COMPARISON OF THE VALENCE BAND OF THE Mn/GeTe, Mn/GeMnTe AND Mn/GeEuTe LAYERS

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*Keywords: photoemission spectroscopy, synchrotron radiation, IV-VI semiconductors, Fano resonance*

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Resonant photoemission spectroscopy (RPES) belongs to experimental techniques developed thanks to access to sources of synchrotron radiation. Wide, continuous spectrum of SR enables studying photoemission for photon energies close to a particular intra-system transition. RPES is particularly useful for studying contribution of partly filled shells (*d* or *f*) of transition metals or rare earth elements to the electronic structure of a system. This technique is based on the Fano effect in which rare earth (RE) 4*f* and transition metal (TM) 3*d* electrons are locally and selectively excited when the photon energy is tuned to the RE 4*d*→4*f* and TM 3*p*→3*d* transition. The photoemission intensity in the resonance region is described by the Fano line shape [1], which consists of a resonance maximum and an antiresonance minimum. Comparison of the spectra measured for these two photon energies allows determination of *f*- and *d*-related emission.

The comparison of the experimental results, which have been received in the photoemission study of electronic structure of GeTe doped with Mn and/or Eu, is presented in this work. The IV-VI crystals are known to form solid solutions not only with magnetic ions with uncompletely filled 3*d* shell (e.g. Mn, Fe), but also with the elements with uncompletely filled 4*f* shell (e.g. Eu, Gd) [2]. Eu-doped IV-VI crystals can be effectively applied for the construction of mid-infrared tunable detectors and lasers. In Eu-doped IV-VI crystals, Eu ions interact ferromagnetically via the RKKY mechanism. The substitutional europium ions occur as Eu<sup>2+</sup>, however, sometimes Eu<sup>3+</sup> can also be detected, especially at disordered surfaces. Presence of Eu<sup>3+</sup> related spectra features indicates a deviation from stoichiometry.

Ge<sub>1-x</sub>Mn<sub>x</sub>Te becomes ferromagnetic with a relatively high Curie temperature - 140 K. *T*<sub>C</sub> of Ge<sub>1-x</sub>Mn<sub>x</sub>Te depends strongly on Mn concentration [3]. However the introduction of Eu ions to the system leads to a similar Curie temperature but for markedly lower Mn contents [4]. Therefore, the properties of Ge<sub>1-x</sub>Mn<sub>x</sub>Te and related systems attract considerable interest, due to possible applications of IV-VI-based systems for fabrication of spintronic devices.

However, Ge<sub>1-x</sub>Mn<sub>x</sub>Te and related solid solutions can be obtained as polycrystalline bulk sample or monocrystalline epilayers. Monocrystalline samples of Ge<sub>1-x-y</sub>Mn<sub>x</sub>Eu<sub>y</sub>Te are not available yet. In order to carry out a thorough, comparative study of all these systems, a set of GeTe, Ge<sub>0.9</sub>Mn<sub>0.1</sub>Te and Ge<sub>0.98</sub>Eu<sub>0.02</sub>Te layers was prepared. The samples were grown on BaF<sub>2</sub> (111) substrates by an MBE method with the use of effusion cells as GeTe, Eu, Te<sub>2</sub> and Mn sources. The substrate temperature was 400-450°C. The content of Mn in Ge<sub>0.9</sub>Mn<sub>0.1</sub>Te and Eu in Ge<sub>0.98</sub>Eu<sub>0.02</sub>Te were checked by energy dispersive X-ray fluorescence analysis. After first photoemission studies of GeTe, Ge<sub>0.9</sub>Mn<sub>0.1</sub>Te, Ge<sub>0.98</sub>Eu<sub>0.02</sub>Te, Mn atoms were introduced into the surface layer of the samples by Mn deposition at room temperature and annealing the sample in ultra high vacuum. In particular, the Ge<sub>1-x-y</sub>Mn<sub>x</sub>Eu<sub>y</sub>Te surface alloy were prepared by this method. Then, the valence bands of the surface alloys were investigated by means of RPES.

The photoemission measurements were performed at the FLIPPER II beamline (E1) in HASYLAB (Germany). The spectra of GeTe, Ge<sub>0.9</sub>Mn<sub>0.1</sub>Te, Ge<sub>0.98</sub>Eu<sub>0.02</sub>Te were measured for the photon energy range of 130 - 160 eV (corresponding to Eu 4*d*→4*f* resonance for both Eu<sup>2+</sup> and Eu<sup>3+</sup>) and 30-60 eV (Mn 3*p*→3*d*).

Fig. 1 shows a typical set of energy distribution curves taken at photon energies 50 eV near to the Mn 3*p*-3*d* resonance for clean GeTe, Ge<sub>0.9</sub>Mn<sub>0.1</sub>Te and Ge<sub>1-x</sub>Eu<sub>x</sub>Te samples, after deposition of manganese and after annealing. In the case of the Ge<sub>0.98</sub>Eu<sub>0.02</sub>Te the peak located around 2.0 eV below the Fermi level in the clean sample can be associated with the Eu<sup>2+</sup> 4*f* final state multiplet contribution to the emission from the valence band. The Mn 3*d* states contribution occurred in the upper part of the valence band, with a maximum at the binding energy of about 4.6 eV. Its shape corresponded to that expected for Mn<sup>2+</sup> ions surrounded by six Te ions in the octahedral coordination. Deposition of Mn and annealing the system led to an increase of Mn 3*d* feature intensity without any change in its shape. This proved

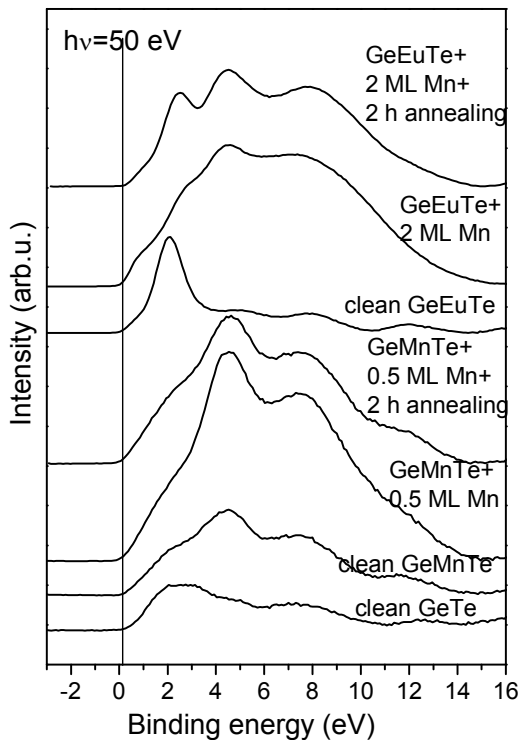


Figure 1. The valence band spectra of GeTe,  $\text{Ge}_{0.9}\text{Mn}_{0.1}\text{Te}$  and  $\text{Ge}_{0.98}\text{Eu}_{0.02}\text{Te}$  measured for clean samples, after deposition of manganese and after annealing, for photon energies 50 eV.

that diffusing Mn ions occupied the same sites in the lattice as those introduced during the layer growth. Increase of Mn contents in the subsurface layer correlates with increase of the sample magnetization. Its relation with magnetic properties of the system is discussed.

For  $\text{Ge}_{1-x-y}\text{Mn}_x\text{Eu}_y\text{Te}$ , the valence band density of states distribution was determined for the first time, to our knowledge. The Mn 3d contribution to the electronic structure of the system was revealed and changes in the Eu-related feature correlated with presence of Mn ions were analyzed.

**Acknowledgements:** The authors acknowledge support by MSHE (Poland) grants N202 101 31/0749 and DESY/68/2007 as well as by the European Community via the Research Infrastructure Action under the FP6 "Structuring the European Research Area" Programme (through the Integrated Infrastructure Initiative "Integrating Activity on Synchrotron and Free Electron Laser Science") at DESY.

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