A COMPARISON OF THE VALENCE BAND STRUCTURE OF BULK AND EPITAXIAL GeTe-BASED DILUTED MAGNETIC SEMICONDUCTORS

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In this work we present a comparison of the experimental results, which have been obtained in the resonant photoemission study of electronic structure of epitaxial layers and bulk crystals of GeTe doped with Mn and/or Eu. Narrow-gap IV–VI semiconductors are known to form solid solutions not only with magnetic ions with partially filled $3d$ shell (*e.g.* Mn, Fe), but also with the elements with partially filled $4f$ shell (*e.g.* Eu, Gd). Such diluted magnetic semiconductors (DMS) exhibit transport, optical and magnetic properties attracting large interest from the point of view of basic research as well as of applications in infrared radiation sources, detectors, thermoelectric generators and, recently, spintronic devices.

The ferromagnetic ordering in IV-VI –based diluted magnetic semiconductors (DMS) is governed by the Ruderman–Kittel–Yoshida–Kasuya interaction mediated by free holes related to native defects. $Ge_{1-x}Mn_xTe$ exhibits ferromagnetic properties with the Curie temperature which is relatively high and strongly dependent on Mn concentration ($T_C \approx 190$ K) [1]. However, the introduction of Eu ions to the system leads to a similar Curie temperature but for markedly lower Mn contents [2]. Therefore, this study was performed in order to reveal Mn $3d$ and Eu $4f$ contributions to the valence band of several GeTe-based DMSs prepared by two different techniques.

The bulk polycrystals of $Ge_{0.86}Mn_{0.14}Te$ and $Ge_{0.4}Mn_{0.5}Eu_{0.1}Te$ were grown by the Bridgman method in the Institute for Problems of Materials Science, National Academy of Sciences of Ukraine. The $Ge_{0.9}Mn_{0.1}Te$, $Ge_{0.98}Eu_{0.02}Te$ and GeTe epilayers were grown on BaF_2 (111) substrates by an MBE method with use of GeTe, Eu, Te_2 and Mn solid sources in the Institute of Physics of the Polish Academy of Sciences (Warsaw, Poland). The substrate temperature was 400-450°C. The chemical composition of the samples was assessed by energy dispersive X-ray fluorescence analysis. Their crystalline structure was determined by X-ray diffraction. Clean sample surfaces for photoemission measurements were prepared *in situ* by scraping the sample with a diamond file under UHV conditions (for polycrystals) or by Ar^+ ion sputtering and annealing (for epilayers). The $Ge_{1-x-y}Mn_xEu_yTe$ surface alloy (for comparison with the $Ge_{0.4}Mn_{0.5}Eu_{0.1}Te$ polycrystal) on a $Ge_{1-x}Eu_xTe$ epilayer was fabricated *in situ* by Mn deposition and annealing under UHV conditions.
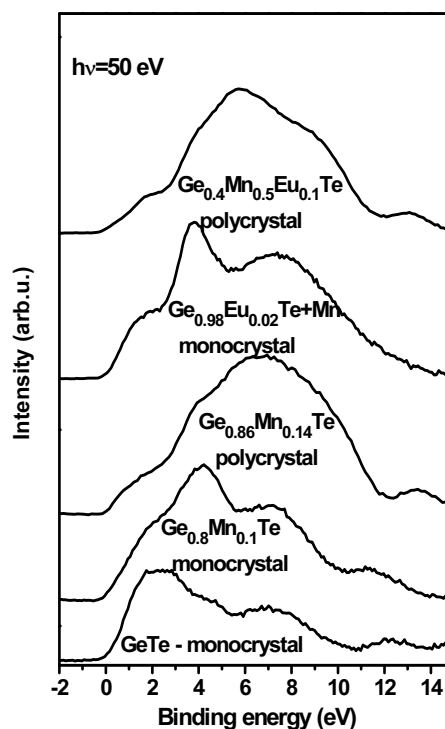

Figure 1. The comparison of the valence band photoemission spectra of GeTe, $Ge_{0.9}Mn_{0.1}Te$, $Ge_{0.98}Eu_{0.02}Te$ + Mn MBE layers and $Ge_{0.4}Mn_{0.5}Eu_{0.1}Te$, $Ge_{0.86}Mn_{0.14}Te$ bulk crystals for photon energy of 50 eV.

The photoemission measurements were performed and photoelectron energy distribution curves were collected in the regime of resonant photoemission after

each stage of the system preparation procedure. All photoemission measurements were made at room temperature with fixed energy resolution of 250 meV. The secondary electron background has been subtracted by means of the Shirley method.

The valence bands of these samples were studied by means of resonant photoemission spectroscopy (RPES). In this technique the radiation energy hv is tuned to the intra-ion electron transition *e.g.* $3p$-$3d$ for transition metal atoms or $4d$-$4f$ for rare earth atoms. Then, the regular photoemission process

$$3p^6 3d^n + hv = 3p^6 3d^{n-1} + e^- \text{ (for TM atoms)}$$

is accompanied by excitation of the ion:

$$3p^6 3d^n + hv = [3p^5 3d^{n+1}]^*.$$

The quantum interference between these two processes leads to autoionization:

$$[3p^5 3d^{n+1}]^* \rightarrow 3p^6 3d^{n-1} + e^-$$

and resonant photoemission described by the Fano formula:

$$I(hv) = I_0 \frac{(q+\varepsilon)^2}{\varepsilon^2 + 1}$$

where q is the symmetry parameter (Fano factor), ε is the reduced energy variable which corresponds to the photon energy in photoemission experiments [3]. RPES is particularly useful for studying the contribution of partially filled shells (d or f) of transition metals or rare earth elements to the electronic structure of DMSs.

This technique is based on the Fano-type *p-d* or *d-f* resonances which lead to strong increase of emission from *d*(*f*) shell and help to reveal related spectral features. The photoemission measurements were performed at the FLIPPER II system in HASYLAB (Hamburg, Germany). The spectra of GeTe, $Ge_{1-x}Mn_xTe$, $Ge_{1-x}Eu_xTe$, $Ge_{1-x-y}Mn_xEu_yTe$ were measured for the photon energy range of 130 - 160 eV (corresponding to Eu $4f \rightarrow 4f$ resonance for both Eu^{2+} and Eu^{3+}) and 30-60 eV (Mn $3p \rightarrow 3d$).

The spectra (photoelectron energy distribution curves) covered the range of electron binding energy starting from the valence band edge down to the Mn $3p$ level. Figure 1 shows a typical set of energy distribution curves taken at photon energy of 50 eV (near the Mn $3p$-$3d$ resonance) for $Ge_{0.96}Mn_{0.14}Te$, $Ge_{0.4}Mn_{0.5}Eu_{0.1}Te$ polycrystal samples, GeTe, $Ge_{0.9}Mn_{0.1}Te$, mocrystalline epilayers and $Ge_{0.98}Eu_{0.02}Te$ surface alloy ($Ge_{0.98}Eu_{0.02}Te$ + Mn). In order to estimate the destiny of state of Mn $3d$ we have to subtract the antyresonace from resonance. The difference spectra of MBE layer we can compare with the difference spectra of bulk samples $Ge_{0.96}Mn_{0.14}Te$ and $Ge_{0.4}Mn_{0.5}Eu_{0.1}Te$. The shape is similar to that reported for $Ge_{1-x}Mn_xTe$ [4].

The valence band density of states distribution of $Ge_{1-x-y}Mn_xEu_yTe$ was determined for the first time, to our knowledge. The change of the Eu $4f$ position induced by introduction of Mn ions, indicating an Mn-Eu interaction, was detected.
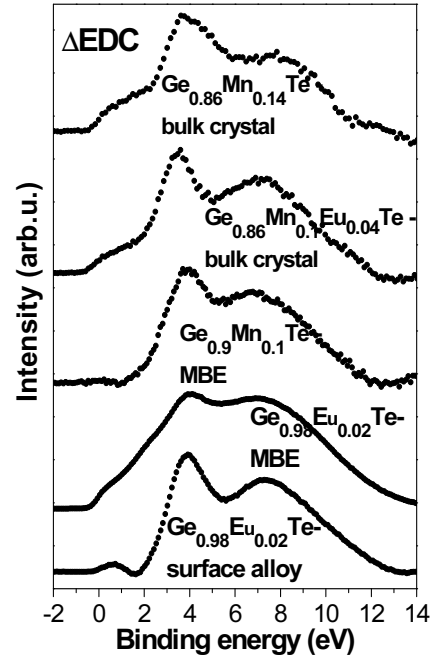

Figure 2. The difference EDCs spectra measured for bulk crystal and MBE layers.

For all investigated systems, the Mn $3d$ states contribution occurred in the upper part of the valence band, with a maximum at the binding energy of about 3.8 eV. Its shape corresponded to that expected for Mn^{2+} ions surrounded by six Te ions in the octahedral coordination.

It was proved that strong, additional feature occurring for polycrystals is non-resonant, and most probably not related to presence of Mn ions. Thus, it is not related to the ferromagnetic behaviour of the bulk crystals.

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