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) governed by the Ruderman–Kittel–Yoshida–Kasuya interaction mediated by free holes related to native defects. Ge₁₋ₓMnₓTe exhibits ferromagnetic properties with the Curie temperature which is relatively high and strongly dependent on Mn concentration (Tᵣ≈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 Ge₀.₉₀Mn₀.₁₄Te and Ge₀.₈₀Mn₀.₂₀Eu₀.₁₀Te were grown by the Bridgman method in the Institute for Problems of Materials Science, National Academy of Sciences of Ukraine. The Ge₀.₈₀Mn₀.₁₀Te, Ge₀.₉₀Eu₀.₀₂Te and GeTe epilayers were grown on BaF₂ (111) substrates by an MBE method with use of GeTe, Eu, Te₂ 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⁺ sputtering and annealing (for epilayers). The Ge₀.₈₀Mn₀.₁₀Eu₀.₀₁Te surface alloy (for comparison with the Ge₀.₉₀Mn₀.₁₀Eu₀.₁₀Te polycrystal) on a Ge₀.₈₀Eu₀.₁₀Te epilayer was fabricated in situ by Mn deposition and annealing under UHV conditions.

![Figure 1](image)

Figure 1. The comparison of the valence band photoemission spectra of GeTe, Ge₀.₈₀Mn₀.₁₀Te, Ge₀.₉₀Eu₀.₀₂Te + Mn MBE layers and Ge₀.₈₀Mn₀.₁₀Eu₀.₁₀Te, Ge₀.₉₀Mn₀.₁₀Te bulk crystals for photon energy of 50 eV.
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 $h\nu$ 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 $3p^63d^n + h\nu = 3p^63d^{n-1} + e^{-} \text{ (for TM atoms)}$ is accompanied by excitation of the ion: $3p^63d^n + h\nu = [3p^53d^{n+1}]^*$. The quantum interference between these two processes leads to autoionization: $[3p^53d^{n+1}]^* \rightarrow 3p^63d^{n-1} + e^{-}$ and resonant photoemission described by the Fano formula:

$$I(h\nu) = I_0 \frac{(q + \epsilon)^2}{\epsilon^2 + 1}$$

where $q$ is the symmetry parameter (Fano factor), $\epsilon$ 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 4d$\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. Fig. 1 shows a typical set of energy distribution curves taken at photon energy of 50 eV (near the Mn 3p-3d resonance) for Ge_{0.9}Mn_{0.1}Te, Ge_{0.9}Mn_{0.1}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 antiresonance from resonance. The difference spectra of MBE layer we can compare with the difference spectra of bulk samples Ge_{0.9}Mn_{0.1}Te and Ge_{0.9}Mn_{0.1}Eu_{0.1}Te. The shape is similar to that reported for Ge_{1.2}Mn_{0.8}Te [4]. The valence band density of states distribution of Ge_{1.2}Mn_{0.8}Eu_{0.2}Te 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.](image)

- 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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