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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 by the resonant photoelectron spectroscopy for a set of selected diluted magnetic semiconductors based on GeTe, doped with manganese. The photoemission spectra are acquired for the photon energy range of 40–60 eV, corresponding to the Mn $3p \rightarrow 3d$ resonances. The spectral features related to Mn $3d$ states are revealed in the emission from the valence band. The Mn $3d$ states contribution manifests itself in the whole valence band with a maximum at the binding energy of 3.8 eV.

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1. Introduction

Narrow-gap IV–VI semiconductors form solid solutions with suitable chalcogenides of magnetic ions with partially filled $3d$ shell (e.g. Mn, Fe), as well as, of the elements with partially filled $4f$ shell (e.g. Eu, Gd). Such diluted magnetic semiconductors (DMSs) exhibit transport, optical and magnetic properties attracting large interest from the point of view of basic research or due to possible applications in infrared radiation sources, detectors, thermoelectric generators and, recently, spintronic devices.

The ferromagnetic ordering in IV–VI-based DMSs is governed by the Ruderman–Kittel–Kasuya–Yoshida (RKKY) interaction mediated by free holes occurring due to the presence of native defects. $\mathrm{Ge}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ exhibits ferromagnetic properties with the relatively high Curie temperature T_C (up to $T_\mathrm{C} \approx 190$ K for $x = 0.08$ [1]). The observed variations of the Curie temperature were ascribed to changes in Mn contents [2] or in carrier density [3]. It was also reported that the introduction of Eu ions enabled a reduction of the Mn contents with retained high Curie temperature [4]. The reported study was performed in order to reveal and compare Mn $3d$ contribution to the valence band of several GeTe-based DMSs, also co-doped with Eu, grown by different techniques. $\mathrm{Ge}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ samples can be grown by the Bridgman technique and by molecular beam epitaxy (MBE). Thus, we compared a bulk polycrystalline sample of $\mathrm{Ge}_{0.86}\mathrm{Mn}_{0.14}\mathrm{Te}$ with an epilayer, with similar Mn contents — $\mathrm{Ge}_{0.9}\mathrm{Mn}_{0.1}\mathrm{Te}$. Since epilayers of $\mathrm{Ge}_{1-x-y}\mathrm{Mn}_x\mathrm{Eu}_y\mathrm{Te}$ were not available yet, such a system was prepared as a surface alloy on the $\mathrm{Ge}_{1-x}\mathrm{Eu}_x\mathrm{Te}$ substrate. Therefore we studied a polycrystalline $\mathrm{Ge}_{0.4}\mathrm{Mn}_{0.5}\mathrm{Eu}_{0.1}\mathrm{Te}$, the epilayer of $\mathrm{Ge}_{0.98}\mathrm{Eu}_{0.02}\mathrm{Te}$ and the $\mathrm{Ge}_{1-x-y}\mathrm{Mn}_x\mathrm{Eu}_y\mathrm{Te}$ surface alloy (grown on $\mathrm{Ge}_{0.98}\mathrm{Eu}_{0.02}\mathrm{Te}$). The GeTe epilayer was measured as a reference system.

2. Experimental details

Bulk polycrystals of $\mathrm{Ge}_{0.86}\mathrm{Mn}_{0.14}\mathrm{Te}$ and $\mathrm{Ge}_{0.4}\mathrm{Mn}_{0.5}\mathrm{Eu}_{0.1}\mathrm{Te}$ were grown by the Bridgman method at the Institute for Problems of Materials Science, National Academy of Sciences of Ukraine. The $\mathrm{Ge}_{0.9}\mathrm{Mn}_{0.1}\mathrm{Te}$, $\mathrm{Ge}_{0.98}\mathrm{Eu}_{0.02}\mathrm{Te}$ and GeTe epilayers were grown on $\mathrm{BaF}_2(111)$ substrates by MBE method with the use of GeTe, Eu, Te, and Mn solid sources, at the Institute of Physics of the Polish Academy of Sciences. The substrate temperature was in the range of 400–450 °C.

The crystal structures of the samples were determined by X-ray diffraction. Their chemical compositions were assessed by energy dispersive X-ray fluorescence analysis. Clean surfaces of polycrystalline samples were prepared *in-situ* by scraping them with a diamond file under ultra high vacuum (UHV) conditions. Surfaces of epilayers were cleaned by repeated cycles of Ar^+ ion sputtering (with the accelerating voltage of 600 V) and by annealing at 250 °C for 2 hours.

The $\mathrm{Ge}_{1-x-y}\mathrm{Mn}_x\mathrm{Eu}_y\mathrm{Te}$ solid solution was prepared *in-situ* as a surface alloy on the $\mathrm{Ge}_{0.98}\mathrm{Eu}_{0.02}\mathrm{Te}$ epilayer.

Two monolayers of Mn were deposited on the substrate and the sample was annealed under UHV conditions.

The resonant photoemission experiments were carried out at the FLIPPER II system in HASYLAB (Hamburg, Germany). The spectra of GeTe, $\mathrm{Ge}_{1-x}\mathrm{Mn}_x\mathrm{Te}$, $\mathrm{Ge}_{1-x}\mathrm{Eu}_x\mathrm{Te}$, and $\mathrm{Ge}_{1-x-y}\mathrm{Mn}_x\mathrm{Eu}_y\mathrm{Te}$ were measured for the photon energy range of 30–60 eV, covering the Fano resonance energy related to the Mn $3p \rightarrow 3d$ transition. In such experiments, the radiation energy is tuned to the intra-ion electron transition (e.g. $3p$–$3d$ for transition metal atoms) and the regular photoemission process (like $3p^6 3d^n + h\nu = 3p^6 3d^{n-1} + \mathrm{e}^-$) is accompanied by excitation of the transition metal ion ($3p^6 3d^n + h\nu = [3p^5 3d^{n+1}]^*$). The quantum interference between these two processes leads to autoionization ($[3p^5 3d^{n+1}]^* \rightarrow 3p^6 3d^{n-1} + \mathrm{e}^-$) and to the resonant photoemission described by the Fano formula

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

where q is the symmetry parameter (Fano factor), ε is the reduced energy variable which corresponds to the photon energy in photoemission experiments [5].

3. Results and discussion

Figure 1 shows a set of resonant photoemission spectra (energy distribution curves — EDC) collected for clean surfaces of $\mathrm{Ge}_{0.96}\mathrm{Mn}_{0.14}\mathrm{Te}$ and $\mathrm{Ge}_{0.4}\mathrm{Mn}_{0.5}\mathrm{Eu}_{0.1}\mathrm{Te}$ polycrystalline samples, GeTe, $\mathrm{Ge}_{0.9}\mathrm{Mn}_{0.1}\mathrm{Te}$ monocrystalline epilayers, $\mathrm{Ge}_{0.98}\mathrm{Eu}_{0.02}\mathrm{Te}$ layer covered with 2 ML of Mn ($\mathrm{Mn/Ge}_{0.98}\mathrm{Eu}_{0.02}\mathrm{Te}$), and $\mathrm{Ge}_{1-x-y}\mathrm{Mn}_x\mathrm{Eu}_y\mathrm{Te}$ surface alloy (annealed $\mathrm{Mn/Ge}_{0.98}\mathrm{Eu}_{0.02}\mathrm{Te}$). The curves were taken for the photon energy of 50 eV (near the Mn $3p$–$3d$ resonance) with a total energy resolution of 250 meV. The measurements were made at room temperature. The origin of the binding energy axis was set at the Fermi energy, determined for a reference metallic sample. The secondary electron background has been subtracted by means of the Shirley method. The spectra covered the range of electron binding energy corresponding to the valence band region. The curves acquired for the $\mathrm{Ge}_{1-x-y}\mathrm{Mn}_x\mathrm{Eu}_y\mathrm{Te}$ surface alloy (Fig. 1, curve 1), the $\mathrm{Mn/Ge}_{0.98}\mathrm{Eu}_{0.02}\mathrm{Te}$ system (Fig. 1, curve 2), and the $\mathrm{Ge}_{0.9}\mathrm{Mn}_{0.1}\mathrm{Te}$ layer (Fig. 1, curve 3) differ markedly from the spectrum of pure GeTe (Fig. 1, curve 0) and consist of three main spectral features: a shoulder at 0–2 eV, the peak at 3.8 eV and a broad maksimum at 6–10 eV. These features do not appear in the spectra of $\mathrm{Ge}_{0.4}\mathrm{Mn}_{0.5}\mathrm{Eu}_{0.1}\mathrm{Te}$ (Fig. 1, curve 4) and $\mathrm{Ge}_{0.86}\mathrm{Mn}_{0.14}\mathrm{Te}$ (Fig. 1, curve 5) polycrystals — the shoulder at 3.8 eV can only be resolved. Intensities of the three features in curves 1–3, as well as, the shoulders in curves 4 and 5 depend on the photon energy, with maximum at 50–51 eV. Such a behaviour, consistent with the occurrence of Mn $3p$–$3d$ resonance, indicates that these features are related to emission from Mn $3d$. The spectral features revealed in curves 1–3 correspond well to those characteristic of resonant emission from the $3d$ shell of the Mn^{2+} ion surrounded by six Te anions with octahedral coordination, like in MnTe [6].

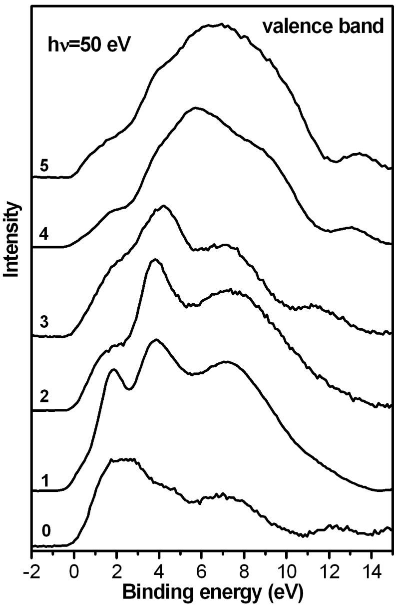

Fig. 1. Valence band photoemission spectra taken for the photon energy of 50 eV: 0 — GeTe monocrystalline MBE layer, 1 — $\mathrm{Ge}_{1-x-y}\mathrm{Mn}_x\mathrm{Eu}_y\mathrm{Te}$ surface alloy, 2 — $\mathrm{Mn/Ge}_{0.98}\mathrm{Eu}_{0.02}\mathrm{Te}$, 3 — $\mathrm{Ge}_{0.9}\mathrm{Mn}_{0.1}\mathrm{Te}$ MBE layer, 4 — $\mathrm{Ge}_{0.4}\mathrm{Mn}_{0.5}\mathrm{Eu}_{0.1}\mathrm{Te}$ polycrystal, 5 — $\mathrm{Ge}_{0.86}\mathrm{Mn}_{0.14}\mathrm{Te}$ polycrystal.

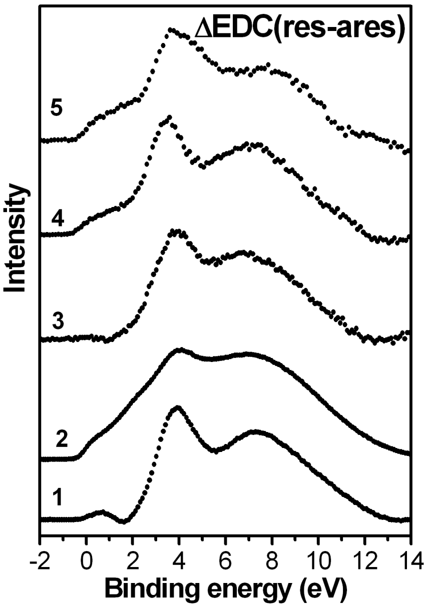

Fig. 2. Differences between the resonant and antiresonant spectra (ΔEDCs) obtained for: 1 — $\mathrm{Ge}_{1-x-y}\mathrm{Mn}_x\mathrm{Eu}_y\mathrm{Te}$ surface alloy, 2 — $\mathrm{Mn/Ge}_{0.98}\mathrm{Eu}_{0.02}\mathrm{Te}$, 3 — $\mathrm{Ge}_{0.9}\mathrm{Mn}_{0.1}\mathrm{Te}$ MBE layer, 4 — $\mathrm{Ge}_{0.4}\mathrm{Mn}_{0.5}\mathrm{Eu}_{0.1}\mathrm{Te}$ polycrystal, 5 — $\mathrm{Ge}_{0.86}\mathrm{Mn}_{0.14}\mathrm{Te}$ polycrystal.

The additional contribution which obscures emission from Mn 3*d* in the spectra of the polycrystalline samples is non-resonant. Thus, it can not be related to precipitates of any other manganese compound. Such species would give a resonant contribution, like MnO [7, 8].

Figure 2 shows the difference spectra (ΔEDC) obtained by subtraction of curves taken at the antiresonance photon energy (47 eV) from those acquired at resonance. Shapes of the obtained curves correspond to the distribution of Mn 3*d* states in the investigated systems. All the difference spectra consist of above mentioned three parts characteristic of the emission from the 3*d* shell of Mn^{2+} ions markedly hybridized with the orbitals of ligands [6]. For $\mathrm{Ge}_{1-x-y}\mathrm{Mn}_x\mathrm{Eu}_y\mathrm{Te}$, the low binding energy part of the difference spectrum is modified due to strong contribution of Eu 4*f* emission, also dependent on the photon energy. The overall shape of curves is also consistent with that reported for $\mathrm{Ge}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ by Senba et al. [9].

4. Conclusions

Distributions of electronic states in valence bands of: polycrystalline $\mathrm{Ge}_{0.86}\mathrm{Mn}_{0.14}\mathrm{Te}$, $\mathrm{Ge}_{0.9}\mathrm{Mn}_{0.1}\mathrm{Te}$ epilayer, polycrystalline $\mathrm{Ge}_{0.4}\mathrm{Mn}_{0.5}\mathrm{Eu}_{0.1}\mathrm{Te}$, $\mathrm{Ge}_{0.98}\mathrm{Eu}_{0.02}\mathrm{Te}$ epilayer covered with Mn and $\mathrm{Ge}_{1-x-y}\mathrm{Mn}_x\mathrm{Eu}_y\mathrm{Te}$ surface alloy were determined by means of resonant photoemission spectroscopy. It was shown that the Mn 3*d* contribution to the valence band corresponds to that expected for Mn^{2+} ions surrounded by Te ions in the octahedral coordination. It was also proved that strong additional emission observed for polycrystals is non-resonant, and it is not related to the presence of Mn ions.

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