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Photoemission Study of Mn 3*d* Electrons in the Valence Band of Mn/GeMnTe

M.A. Pietrzyk, B.J. Kowalski, B.A. Orłowski, W. Knoff,
V. Osinniy, I.A. Kowalik, T. Story

Institute of Physics, Polish Academy of Sciences
al. Lotników 32/46, 02-668 Warsaw, Poland

and R.L. Johnson

Institute of Experimental Physics, University of Hamburg
Luruper Chaussee 149, 22761 Hamburg, Germany

We present the results of the electronic band structure study of $Ge_{0.9}Mn_{0.1}Te$ epilayers, clean and modified *in situ* by deposition of manganese atoms. The sets of resonant photoemission spectra were measured for the photon energy range covering the energy of Mn $3p \to 3d$ transition ($45 < h\nu < 60$ eV). They were acquired for the clean surface of the $Ge_{0.9}Mn_{0.1}Te$ sample, after evaporation of 0.5 monolayer Mn and after annealing (at 200°C) inducing diffusion of Mn atoms into the $Ge_{0.9}Mn_{0.1}Te$ crystal. The Mn 3*d* contribution to the emission from the valence band of $Ge_{0.9}Mn_{0.1}Te$ was determined and the strength of interaction between Mn and its ligands was discussed.

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1. Introduction

$Ge_{1-x}Mn_xTe$ belongs to IV–VI-based diluted magnetic semiconductors (DMS), in which the presence of magnetic ions and their exchange interaction with carriers in the conduction and valence bands result in unusually strong magneto-transport and magneto-optic phenomena. Such systems can be formed by doping with either transition metals (like Mn) or rare earth elements (Eu, Gd, Ce, Yb) [1]. Some IV–VI DMSs, with high hole concentrations ($p \approx 10^{21}$ cm^{-3}), exhibit ferromagnetic properties at low temperatures [2] due to the Ruderman–Kittel–Kasuya–Yoshida interaction. $Ge_{1-x}Mn_xTe$ is a ferromagnet with a relatively high Curie temperature (up to 140 K) strongly depending on Mn concentration [3]. At approximately $x = 0.5$ the Curie temperature reaches a maximum and then decreases probably due to increasing antiferromagnetic interaction. Thus, the investigation of its properties, including the band structure, attracts a considerable interest, in view of possible applications of IV–VI-based systems in fabrication of spintronic devices.

Our previous studies of the electronic structure of $\mathrm{Ge}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ and $\mathrm{Ge}_{1-x-y}\mathrm{Mn}_x\mathrm{Eu}_y\mathrm{Te}$ bulk polycrystals grown by a Bridgman method showed unexpectedly a low photoemission from Mn $3d$ states under Mn $3p$–$3d$ resonance conditions (characteristic of Mn^{2+} ions), inconsistent with crystal composition and results of non-resonant photoemission measurements [4]. Spin-echo experiments also suggested that a mixed valence state may exist in the system, with Mn ions other than Mn^{2+} [5]. In search for verification of these observations and a consistent description of the electronic structure of $\mathrm{Ge}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ we performed a photoemission study of $\mathrm{Ge}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ prepared under different conditions, so having a different structural quality and also magnetic properties. We investigated the electronic structure of $\mathrm{Ge}_{0.9}\mathrm{Mn}_{0.1}\mathrm{Te}$ epitaxial, monocrystalline layers grown by MBE. The results are reported in this paper.

The experimental method used in the study was the resonant photoemission spectroscopy (RPES). In this technique the radiation energy is tuned to intra-ion resonant electron excitation, like $3p$–$3d$ for transition metal atoms. The relaxation of the excited ions leads to the emission of electrons in a process

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

$$({}^* \ - \ \text{excited state}).$$

Quantum interference between the process involving intra-ion excitation to discrete states and the regular photoemission to continuum states with free electrons

$$\mathrm{Mn}\ 3p^6 3d^n + h\nu \rightarrow \mathrm{Mn}\ 3p^6 3d^{n-1} + \mathrm{e}^-$$

leads to a Fano-type resonance [6]. In particular, it manifests itself in enhancement of Mn $3d$ related emission for photon energies close to the Mn $3p$–$3d$ transition. Therefore, we applied resonant photoemission spectroscopy in order to determine the electronic states distribution in $\mathrm{Ge}_{1-x}\mathrm{Mn}_x\mathrm{Te}$, in particular the Mn $3d$-related contribution to the valence band. The results are compared with those acquired previously for related bulk crystals.

2. Experimental details

The $\mathrm{Ge}_{0.9}\mathrm{Mn}_{0.1}\mathrm{Te}$ layers were grown on BaF_2 (111) substrates by an MBE method with the use of effusion cells as GeTe, Te_2, and Mn solid sources. The substrate temperature was 400–450°C. The contents of Mn in the layer was checked by energy dispersive X-ray fluorescence analysis. The sample surface was protected by a layer of amorphous tellurium.

The resonant photoemission experiments were performed at the synchrotron radiation facility HASYLAB in Hamburg (Germany). Synchrotron radiation obtained from the storage ring DORIS III was monochromatized with the FLIPPER

II plane grating vacuum monochromator designed for the photon energy range of 15–200 eV.

Before the photoemission experiments, the protecting tellurium layer was removed *in situ* by sputtering with Ar^+ ions and annealing under UHV condition. The Mn overlayers were deposited *in situ* at room temperature. The amount of deposited manganese was measured using a quartz microbalance. After each stage of sample treatment (deposition or annealing) the sample was transferred to the analysis chamber and photoemission experiments were carried out. The energy resolution was kept at 250 meV. The origin of the energy axis was set at the Fermi energy as measured for a reference metallic sample.

3. Results and discussion

The goal of this work was to determine the electronic structure of clean $\mathrm{Ge}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ and $\mathrm{Ge}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ covered with a submonolayer of manganese. After Mn deposition the sample was annealed. In order to reveal a contribution of Mn $3d$ states to the valence band of the Mn/GeMnTe system we applied resonant photoemission spectroscopy for photon energies in the range of 45–60 eV (corresponding to Mn $3p \rightarrow 3d$ transition). The spectra (photoelectron energy distribution curves (EDCs)) covered the range of electron binding energy from the valence band edge to 15 eV. The spectra were normalized to the photon flux. The secondary electron background has been subtracted by means of the Shirley method.

Figure 1 shows the photoelectron energy distribution curves taken at several photon energies near to the Mn $3p$–$3d$ resonance. A strong resonant enhancement of the emission from the valence band and appearance of a maximum at 4.7 eV was observed for $\mathrm{Ge}_{0.9}\mathrm{Mn}_{0.1}\mathrm{Te}$ at the photon energy of 50 eV. The antiresonance behaviour (suppression of the Mn $3d$-related emission) was observed at $h\nu = 47$ eV.

Figure 2 shows the comparison of the valence band spectra taken at $h\nu =$ 50 eV (under Mn $3p$–$3d$ resonance conditions) for clean GeTe, $\mathrm{Ge}_{0.9}\mathrm{Mn}_{0.1}\mathrm{Te}$ before and after Mn deposition as well as after the annealing of the system. In the case of clean GeTe the spectrum consists of three main parts: (1) Te $5p$ states with a contribution of the cation p states (0–5.5 eV), (2) Ge $4s$ states (5.5–10.5 eV), and (3) Te $5s$ states (10.5–14 eV) [6].

In the case of clean $\mathrm{Ge}_{0.9}\mathrm{Mn}_{0.1}\mathrm{Te}$ (Fig. 2) one can see the Mn $3d$ contribution with three features: at the binding energy of about 4.7 eV, 7.3 eV, and 11.3 eV. Its overall shape corresponds to that expected for a system with Mn^{2+} ions surrounded by six Te ions in the octahedral coordination [7]. The main feature of the valence band of GeTe may contribute to the shoulder at the leading edge of the spectrum, other features related to GeTe are covered by the manganese-related emission. The deposition of Mn has led to an increase in intensity of the Mn $3d$ features. The overall shape of the spectrum remains similar but the features in the high energy part of the spectrum are less discernible (Fig. 2).

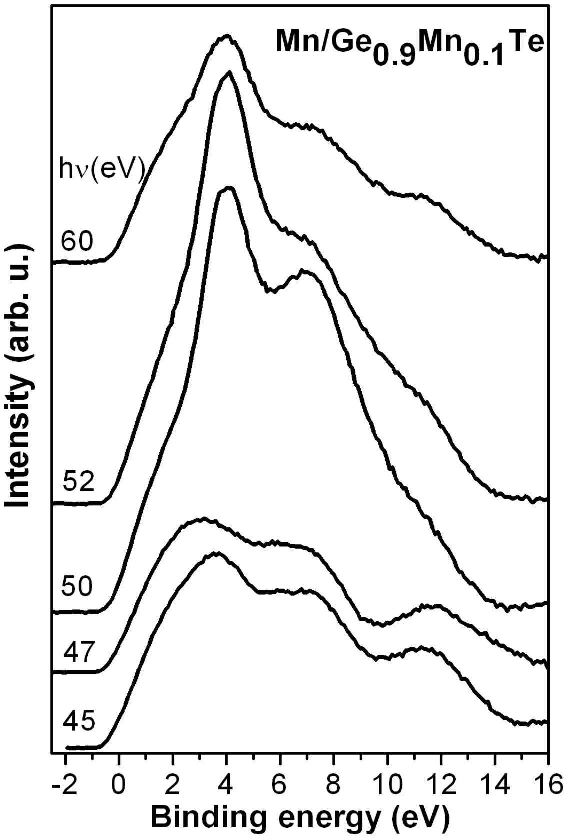

Fig. 1. The valence band spectra of $Ge_{0.9}Mn_{0.1}Te$ measured after deposition of 0.5 ML Mn, for photon energies near the Mn $3p$–$3d$ excitation threshold.

After annealing the $Mn/Ge_{0.9}Mn_{0.1}Te$ system (at 200°C for 2 hours) the spectra became very similar to the curves obtained before the evaporation of manganese. The intensity of the photoemission decreased, probably due to diffusion of surface manganese atoms into the sample. Nevertheless, the Mn related emission remained markedly stronger than for $Ge_{0.9}Mn_{0.1}Te$. The close similarity between the spectra of $Ge_{0.9}Mn_{0.1}Te$ and annealed $Mn/Ge_{0.9}Mn_{0.1}Te$ proved that Mn ions diffusing from the overlayer into the sample occupied the same sites in the lattice as those introduced during the layer growth.

In order to determine the contribution of the Mn $3d$ shell to the valence band of the investigated system, we calculated a difference of the photoemission spectra taken at resonance ($h\nu = 50$ eV) and antiresonance ($h\nu = 47$ eV) photon energies (Fig. 3). The Mn $3d$-related emission extends from 0 to 15 eV binding energy and it has a dominant maximum at about 4.7 eV below the Fermi level.

The overall shape of the Mn $3d$ contribution to the valence band photoemission (Fig. 3) is consistent with that characteristic of emission from Mn $3d$ states

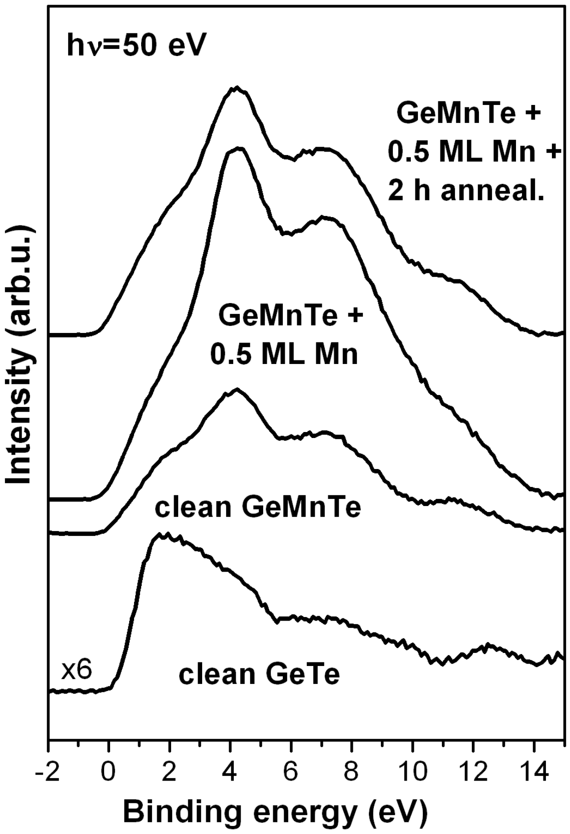

Fig. 2. The EDCs measured for clean GeTe, clean $Ge_{0.9}Mn_{0.1}Te$, $Ge_{0.9}Mn_{0.1}Te$+ 0.5 ML Mn, and $Ge_{0.9}Mn_{0.1}Te$ +0.5 ML Mn+2 hour annealing at 200°C.

in various DMSs [8, 9]. It consists of the main maximum (at 4.7 eV), a satellite structure observed for higher binding energies, and a structure above the main maximum (for lower binding energies). However, the structure overlapping with the upper part of the valence band is very weak, in comparison with that measured for bulk GeMnTe [4] or DMSs with zinc-blende structure. This part of the spectrum can be relatively weaker for Mn ions in an octahedral coordination [7], in comparison with the results obtained for systems with tetrahedral coordination [8, 9]. On the other side, the calculation carried out within the configuration interaction (CI) cluster model [9] proved that intensities of the three main parts of the Mn 3*d* photoemission spectrum depend on the relative positions of Mn 3*d* and anion *p* states, Mn 3*d* electron correlation energy, and hybridization of *d* and *p* states. In particular, the intensity ratio of the upper part of the spectrum with respect to the main maximum increases with increasing *p*–*d* hybridization. The "satellite/main" ratio increases with decreasing *p*–*d* hybridization. In accordance with that, the upper part of the spectrum and the major part of the main maxi-

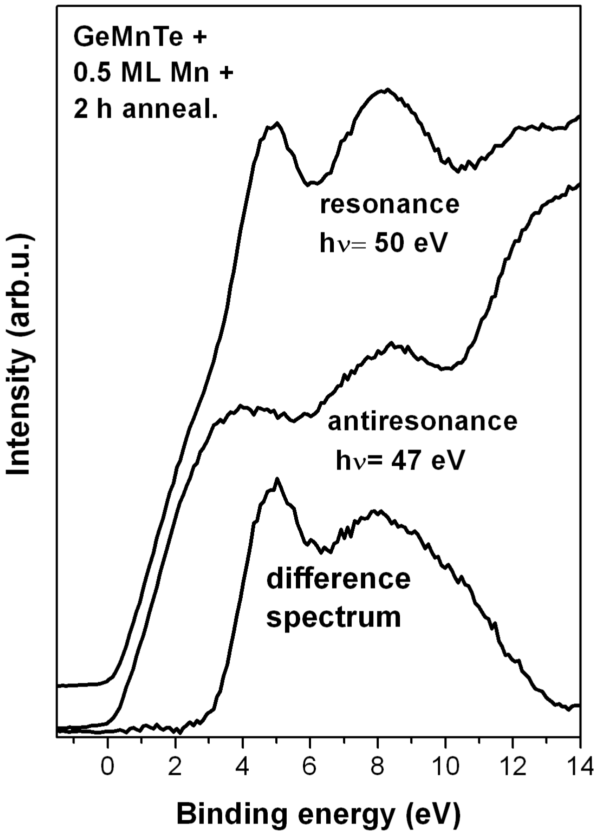

Fig. 3. The resonance–antiresonance difference curve obtained for $Ge_{0.9}Mn_{0.1}Te$ surface covered with 0.5 ML of Mn and annealed at 200°C for 2 hours. The photoemission spectra measured under resonance ($h\nu = 50$ eV) and antiresonance ($h\nu = 47$ eV) conditions are also shown (as measured — prior the secondary electron background subtraction).

mum correspond to emission with $d^5\underline{L}$ final states ($\underline{L}$ denotes a ligand hole). The satellite structure and some contribution to the main maximum occur due to the emission with d^4 final states. As a consequence, the very weak emission in the upper part of the valence band, shown in Fig. 3, together with the relatively weak main maximum (with respect to the satellite structure), suggests that p–d hybridization is weak in the studied layers, in comparison with that in zinc-blende DMS (like CdMnTe [8] or CdMnY (Y = S, Se, Te) [9]) or in polycrystalline bulk GeMnTe.

4. Summary

A resonant photoemission study of the electronic structure of $Ge_{0.9}Mn_{0.1}Te$ was performed for the photon energy range corresponding to the Mn $3p \rightarrow 3d$ excitation. The analysis of the valence band spectra of clean $\mathrm{Ge_{0.9}Mn_{0.1}Te}$ sample and the sample modified *in situ* by deposition of 0.5 ML of Mn enabled us to determine the Mn 3d contribution to the valence band of the system. The annealing of the system (at 200°C) led to diffusion of manganese atoms into the sample and substitution of them into the lattice of $\mathrm{Ge_{0.9}Mn_{0.1}Te}$. Analysis of the shape of the Mn 3d contribution to the emission from the valence band suggests that $p-d$ hybridization in the studied system is weaker than in other DMSs and even in the previously studied bulk $\mathrm{Ge}_{1-x}\mathrm{Mn}_x\mathrm{Te}$.

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